Structurally stabilized olivine lithium phosphate cathodes with enhanced electrochemical properties through Fe doping†

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Controlling the crystallographic structure in olivine lithium phosphates is crucial for obtaining superior electronic (J. Electrochem. Soc., 2002, 149, A1184–A1189) and ionic conductivities (Electrochem. Solid-State Lett., 2006, 9, A352–A355; Electrochem. Solid-State Lett., 2006, 9, A439–A442; Nat. Mater., 2002, 1, 123–128), and stability, for use as cathodes in lithium batteries. Here, we report a completely new approach to enhance Li⁺ extraction and transport in LiCoPO₄ through Fe doping. We show that preferential Fe occupation of the 4c sites suppresses 4a–4c antisite mixing of Li and Co, thereby stabilizing the olivine structure by compensating for the Co-encapsulating oxygen octahedron shrinkage due to Co⁺ oxidation during Li⁺ extraction. The structural stabilization gives rise to ~10% higher charge capacity at a two-fold lower resistance than the undoped counterparts besides accelerating the intercalation/extraction kinetics. Our findings provide key atomistic-level insights that pave the way for the rational design and realization of new types of metal-doped cathode materials for lithium batteries and related applications.

Introduction

Growing universal demands for electric and hybrid electric vehicles necessitate the development of lithium ion batteries with high energy storage and power delivery characteristics.1,2 Although LiCoO₂ is the most widely used cathode in extant lithium batteries, the low structural and thermal stabilities of this material render it inadequate for next generation applications entailing higher temperatures and more aggressive conditions. Olivine-structured transition metal lithium phosphates LiMPO₄ (M = Fe, Co, Mn, and Ni) are promising replacements for LiCoO₂ because they exhibit practical discharge capacities as high as ~170 mA h g⁻¹ and good thermal stability under severe conditions.3,4 Amongst the LiMPO₄ family, LiFePO₄ and LiCoPO₄ are particularly attractive candidates with high structural and thermal stabilities of LiCoO₂ cathodes render them inadequate for use in next generation applications. Olivine-structured transition metal lithium phosphates are promising replacements due to their theoretical discharge capacities as high as ~170 mA h g⁻¹ and good thermal stability under severe conditions, but are limited by low Li⁺ ion conductivity. A completely new approach—underpinned by ab initio calculations, absorption spectroscopy and diffraction—to enhance Li⁺ transport in LiCoPO₄ by creating wider channels for Li⁺ transport through Fe doping provides key atomistic-level insights that pave the way for the rational design and realization of new types of metal-doped cathode materials for lithium batteries and related applications. Hence, these findings can solve general issues in not only olivine-structured phosphate but also other cathode materials applicable to HEV and energy storage system for renewable energy.

Broader context

Growing demands for electric vehicles necessitate the development of lithium ion batteries with high energy storage and power delivery characteristics. The low structural and thermal stabilities of LiCoO₂ cathodes render them inadequate for use in next generation applications. Olivine-structured transition metal lithium phosphates are promising replacements due to their theoretical discharge capacities as high as ~170 mA h g⁻¹ and good thermal stability under severe conditions, but are limited by low Li⁺ ion conductivity. A completely new approach—underpinned by ab initio calculations, absorption spectroscopy and diffraction—to enhance Li⁺ transport in LiCoPO₄ by creating wider channels for Li⁺ transport through Fe doping provides key atomistic-level insights that pave the way for the rational design and realization of new types of metal-doped cathode materials for lithium batteries and related applications. Hence, these findings can solve general issues in not only olivine-structured phosphate but also other cathode materials applicable to HEV and energy storage system for renewable energy.
complementary advantages. LiFePO 4 is inexpensive and offers high Li + intercalation/de-intercalation reversibility as well as excellent thermal stability, but suffers from a low energy density (e.g., ~580 Wh kg −1) due to a low Li intercalation potential (Fe 3+/Fe 2+ , 3.45 V vs. Li +/Li). LiCoPO 4 has a very high theoretical energy density of 800 Wh kg −1 due to a high intercalation potential (Co 3+/Co 2+ , 4.80 V vs. Li +/Li), but is limited by low electronic and Li + ionic conductivity.

Although surface carbon coating can increase the electronic conductivity of LiCoPO 4, the low Li + ion conductivity ultimately limits the discharge capacity to below 110 mA h g −1. Consequently, many studies have focused on facilitating Li + ionization and transport, e.g., by shortening diffusion paths through the use of nanostructured LiCoPO 4 or expanding transport channels along the [010] direction of the olivine crystal and manipulating the transition metal oxidation state through doping. While Cu, Cr and Ni doping improves the electrochemical performance of LiCoPO 4, doping-induced atomic-scale changes in structure and composition of LiCoPO 4 that lead to enhanced properties are yet to be revealed and fully exploited.

Recent theoretical work suggests that antisite defects in the olivine crystal, e.g., involving the 4a site meant for Li + and the 4c site meant for the transition metal, are key determinants of electrochemical reactivity in LiMPO 4, but have not been experimentally verified.

Here, we combine the complementary properties of LiCoPO 4 and LiFePO 4 by doping LiCoPO 4 with Fe to obtain a dramatic enhancement in reversible Li + intercalation and extraction compared with pristine LiCoPO 4. We show by ab initio calculations combined with near edge X-ray absorption spectroscopy (XANES), extended X-ray absorption fine structure spectroscopy (EXAFS) and neutron scattering measurements that the preferred occupancy of Fe dopants in the 4c site of Co suppresses antisite occupancy of Li and Co in 4a and 4c sites, and stabilizes the olivine structure during Li extraction. Expansion of the Co-encapsulating oxygen octahedra due to Fe doping compensates for the structure destabilizing shrinkage due to Co 3+ oxidation during Li extraction and widens the [010] Li + transport channels. These effects lead to ~10% higher charge capacity at a two-fold lower resistance than the undoped counterparts besides accelerating the intercalation/extraction kinetics. These results provide insights that pave the way for the rational design of new types of metal-doped cathode materials for lithium batteries and related applications. We first outline the theoretical basis for Fe-doping and its effects, followed by corroborating experimental evidence. We then demonstrate via the results of charge-discharge testing of batteries that Fe-doped olivine lithium cobalt phosphate electrodes exhibit significantly higher Li + transport than the undoped ones.

Results and discussion

Table 1 summarizes results of total energy calculations and full structural optimization for LiCoPO 4 and LiFePO 4 to identify the main factors determining the structural stability and Li + diffusion channel size in olivine-structured lithium phosphates. The measured lattice parameters are within 2% of the theoretical predictions. The total transition magnetic moment is zero in both compounds for the antiferromagnetic configuration, which yields lower total energies than the ferromagnetic configuration, in good agreement with the experiment and prior first-principles calculations. Examination of the magnetic moments of individual transition-metal ions (see Table 1) shows that the high-spin configuration is the stable state for both compounds.

Fig. 1 plots the local density of states (DOS) for the transition metals in LiCoPO 4 and LiFePO 4. We note that the major spin states are identical to the minor spin states for the AFM configuration. The calculated band gaps were 3.4 eV for LiCoPO 4 and 1.9 eV for LiFePO 4. The states between ~8 eV and the Fermi level are mainly comprised of the 3d orbitals of the transition metals in LiCoPO 4 and LiFePO 4. The anti-ferromagnetic configuration was considered in all our calculations.

<table>
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<th>Composition</th>
<th>Approximation</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>V/Å 3</th>
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transition metals. In LiCoPO_4 we observe a broad band of states consisting of hybridized t_2g and e_g orbitals below the Fermi level, without any discernable band splitting near the Fermi level. In contrast, LiFePO_4 exhibits a peak in the filled e_g states close to the Fermi level, well separated by a ~1.2 eV gap from the 3p-e_g hybridized broad band states below. The magnitude of this band separation generally depends on the ionic radius and oxidation state of the metal center. The larger Shannon ionic radius for Fe (99 pm) than Co (88.5 pm) in O^- octahedra in the high-spin state implies a larger octahedral-site stabilization energy (OSSE) for Fe^2+ than Co^2+ ions and a larger orbital splitting in Fe-doped LiCoPO_4. These results are in accordance with previously calculated OSSE of LiFePO_4 and LiCoPO_4 and suggest that Fe^2+ substitutes Co^2+ in the 4a sites, as supported by our XANES measurements described below. The larger volume of the Co-encapsulating octahedron gives rise to a larger Li^+-Li^+ separation than in undoped LiCoPO_4, leading to orbital splitting and a wider Li^+ transport path along [010].

We synthesized Fe-doped LiCoPO_4 by solid state reaction of Li_2PO_4, Fe(PO_4)_2·8H_2O, and Co_3(PO_4)_2·8H_2O. X-Ray absorption near edge spectra at the Co K-edge (see Fig. 2a) reveal that the Co 1s → 4p white line remains essentially unchanged upon Fe doping. The dipole forbidden pre-edge peaks attributable to Co 1s → 3d transition also track the white line (inset, Fig. 2a), and indicate the retention of the Co^2+ state seen in CoCO_3—a compound with oxidation and coordination states similar to LiCoPO_4. The first three peaks of the radial distribution functions for LiFePO_4 and LiCo_0.9Fe_0.1PO_4 yield Co–O, Co–P, and Co–Co bond distances that are in good agreement with those obtained from EXAFS analysis (Table 2b). Considering that LiCoPO_4 is composed of a distorted hcp framework that contains Li and Co in octahedral sites and P in tetrahedral sites, the Li^+ and Co^2+ may selectively occupy the 4a (0, 0, 0) and 4c (x, 1/4, z) sites respectively (O-model), or co-occupy the two sites (D-model). The strong covalent bond between O^2- and P^5+ precludes Li^+ and Co^2+ from occupying the tetrahedral sites. Rietveld refinement of neutron diffractograms from LiCoPO_4 and LiCo_0.9Fe_0.1PO_4 reveals that the D-model configuration is slightly preferred over the O-model because of a better agreement with the experimental data. Within the D-model, however, Li and Co atoms preferentially occupy the 4a and 4c sites, respectively (see Tables S1 and S2 and Fig. S1 and S2 in the ESI†). For LiCo_0.95Fe_0.05PO_4 in particular, the Fe almost never occupies the 4a site.

![Fig. 2 X-Ray absorption spectra from pristine and Fe-doped LiCoPO_4.](image)

(a) Calibrated and normalized XANES data at the Co K-edge. Inset shows a blown up version of the Co K pre-edge region. (b) Radial distribution functions for LiFePO_4 and LiCo_1−xFexPO_4 obtained by Fourier transformation of k^4-weighted [k^2χ(k)] Co EXAFS data. (c) d(atomic distance)/dE vs. E (photon energy) plot near the Fe K edge for LiFePO_4 and LiCo_0.9Fe_0.1PO_4, showing the 1s_k and e_g absorption bands. (d) Comparison of the Fe K edge for LiCo_0.95Fe_0.05PO_4 and LiCo_0.9Fe_0.1PO_4.

Table 2 Co–O inter-atomic distances obtained (a) from the FEFF fit to the EXAFS data and (b) from Rietveld refinement of the X-ray diffractograms for pristine and Fe-doped LiCoPO_4

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<th>Co–O(1)</th>
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<th>Co–O(3)</th>
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The antisite mixing of Li\(^+\) and Co\(^{2+}\) between 4\(\alpha\) and 4\(c\) positions in LiCoPO\(_4\) and LiCo\(_{0.95}\)Fe\(_{0.05}\)PO\(_4\) was analysed using a combination of Rietveld refinement and the maximum entropy method (MEM).\(^{29,17}\) The nuclear density distributions on the (002) plane for LiCoPO\(_4\) and LiCo\(_{0.95}\)Fe\(_{0.05}\)PO\(_4\) (see Fig. 3c and d) show Li atoms at \(z = 0.5\), with higher nuclear densities for the Fe-doped compound. This result implies that Fe doping contributes to maintaining the inherent occupancies of Li and Co in the crystal lattice. The much higher OSSE invoked from crystal field theory for Fe\(^{2+}\) (\(d^6\) \(t_{2g}^6\) \(e_g^1\)) as described earlier in Fig. 1 enhances the stability of the oxygen octahedron in LiFePO\(_4\).\(^{30,31}\) Thus, suppression of mixed occupancy of Li\(^+\) and Co\(^{2+}\) at 4\(\alpha\) and 4\(c\) sites is an important consequence of Fe doping by which the stability of the olivine structure is enhanced (Fig. 4).

We characterized the electrochemical properties of carbon-coated composites fabricated from LiCo\(_{1-x}\)Fe\(_x\)PO\(_4\) samples with \(x = 0\) and 0.05 to verify if Fe-induced structural stabilization of the oxygen octahedron by suppressed antisite mixing results in improved electrochemical performance. Galvanostatic measurements show distinctly different charge–discharge curve shapes and voltage plateau evolution for the two composites. In particular, Fe-doped composites show distorted curves during initial charging (Fig. 5a) with a slightly lower average charging voltage and a \(\sim 10\%\) higher initial charging capacity of 120 mA h g\(^{-1}\) than pure LiCoPO\(_4\) (108 mA h g\(^{-1}\)) indicating that Fe is electrochemically active during Li\(^+\) extraction. Fe doping also improves the kinetics of Li intercalation/de-intercalation as indicated by the decreased hysteresis in the charge–discharge voltage plateaus with increasing Fe content resulting in enhanced the cyclic property and rate capability of LiCoPO\(_4\) (Fig. S3†). The electrode resistances of the composites during the first charge were estimated from the open- and close-circuit voltage profiles (see Fig. 5b and c) obtained by procedures described elsewhere.\(^{32}\) The electrode resistance during the first Li\(^+\) extraction was very high at \(\sim 123\) MW for LiCoPO\(_4\) while LiCo\(_{0.95}\)Fe\(_{0.05}\)PO\(_4\) exhibits a more than two-fold lower initial resistance around 48 M. In addition, a chronoamperometric test showed that Fe doping enhances Li diffusivity from \(\sim 10^{-12}\) (cm\(^2\) s\(^{-1}\)) to \(\sim 10^{-10}\) (cm\(^2\) s\(^{-1}\)) in accordance with the structural discussion. Such significant decrease in initial resistance and increase in Li diffusivity correlate well with the wider channels for Li\(^+\) transport in Fe-doped LiCoPO\(_4\).\(^{33}\)

Our theoretical and experimental studies of the local atomic arrangement in the olivine structure described above indicate that diminished antisite mixing between the 4\(\alpha\) site and the 4\(c\) site is responsible for the channel widening and improved Li\(^+\) transport properties. In olivine lithium phosphates, PO\(_4\) tetrahedra straddle adjacent transition metal planes and constrain the free volume of 4\(\alpha\) channels, which serve as conduits for Li\(^+\) transport. Thus, even a small amount of antisite mixing between 4\(\alpha\) and 4\(c\) creates a physical bottleneck and seriously limits Li\(^+\) intercalation capacity and reaction reversibility. Herein, the rational design of Fe-doped LiCoPO\(_4\) based on the crystal field theory stabilizes the oxygen coordination around Co by suppressing 4\(\alpha\)–4\(c\) antisite mixing and facilitates reversible

Fig. 3 Cation occupancy in 4\(\alpha\) and 4\(c\) sites of pristine LiCoPO\(_4\) and Fe-doped LiCoPO\(_4\). (a) Crystal structure and (b) nuclear density distributions of LiCo\(_{0.95}\)Fe\(_{0.05}\)PO\(_4\) calculated by MEM on neutron diffraction data. The negative value corresponds to the nuclear density of the Li atom located at (0.5, 0.5, 0.5) in the unit cell. The coherent scattering length adopted for MEM was –2.2 fm for the Li atom (femtometre is the unit of nuclear length indicating the bound coherent scattering length). Two-dimensional (002) sections and diagonal line profiles of (c) LiCoPO\(_4\) and (d) LiCo\(_{0.95}\)Fe\(_{0.05}\)PO\(_4\) are shown.
Li$^+$ transport, leading to capacities over 120 mA h g$^{-1}$. These results and analyses provide the long-awaited experimental evidence and a new rational pathway for circumventing the low Li$^+$ ion transport rate in olivine-structured materials.

Conclusions

In summary, we have shown using ab initio calculations and absorption spectroscopy that Fe doping suppresses antisite mixing of Li$^+$ and Co$^{2+}$ at 4$a$ and 4$c$ sites in the olivine structure of LiCoPO$_4$ due to a higher stabilization energy of oxygen octahedra that encapsulate Fe preferentially occupying the 4$c$ sites. The resultant expansion of octahedra leads to a proper energy separation of t$_{2g}$ and e$_g$ orbitals in Fe-doped LiCoPO$_4$ without changing the oxidation state of Co. X-Ray and neutron diffractography finally confirm that these structural changes widen the Li$^+$ transport channels. Fe-doping-induced structural stabilization and Li$^+$ ion transport channel enlargement result in a significantly greater capacity and a more than two-fold enhancement in the electro-chemical performance of Li batteries using olivine LiCoPO$_4$ electrodes.

Acknowledgements

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Notes and references