Li-ion storage dynamics in metastable nanostructured Li$_2$FeSiO$_4$ cathode: Antisite-induced phase transition and lattice oxygen participation

Xia Lu$^{a,d,1}$, Hsien-Chieh Chiua$^{a,1}$, Zachary Arthurb$^{1}$, Jigang Zhou$^{c}$, Jian Wang$^{c}$, Ning Chen$^{c}$, De-Tong Jiang$^{b, **}$, Karim Zaghib$^{d, *}$, George P. Demopoulos$^{a, ***}$

$^a$ Materials Engineering, McGill University, Montréal, Québec, H3A 0C5, Canada
$^b$ Department of Physics, University of Guelph, Guelph, Ontario, N1G 2W1, Canada
$^c$ Canadian Light Source, 44 Innovation Boulevard, Saskatoon, S7N 2V3, Canada
$^d$ Institut de recherche d’Hydro-Québec (IREQ), Varennes, Québec, J3X 1S1, Canada

Abstract

Li$_2$FeSiO$_4$ (LFS) has drawn much attention as cathode for high capacity Li-ion batteries. Even though significant volume of study has been devoted to its crystal chemistry and electrochemistry, many questions relating to its Li-ion storage dynamics remain yet to be fully elucidated. In this context, synchrotron-based X-ray diffraction and absorption spectroscopies are employed to characterize the phase stability and charge compensation mechanism in a metastable Li$_2$FeSiO$_4$ nanostructured cathode as a function of state-of-charge (Li$_2$FeSiO$_4$, $x = 0, 0.25, 0.50, 0.75, 1.0$) and cycling at very low current. The results demonstrate (i) no detectable phase transition from monoclinic to orthorhombic phase during the first charge-discharge cycle but rather formation of antisite defects that progressively induce phase transformation after several electrochemical cycles; (ii) characteristics of solid solution Li-ion storage (Li$_2$FeSiO$_4$, $x = 0$–1); and (iii) the charge compensation for the first Li extraction does not come solely from the ferrous to ferric conversion, but interestingly from prominent participation of lattice oxygen as well that appears to destabilize the cycled LFS structure with significant performance implications.

© 2016 Elsevier B.V. All rights reserved.
1. Introduction

Lithium iron orthosilicate materials (Li$_2$FeSiO$_4$ denoted as LFS) are drawing increasingly more attention as a promising type of cathode for next generation Li-ion batteries because of the high theoretical capacity [1–4], nearly two times higher than that of the analogous polyanion cathode LiFePO$_4$ (170 mAh/g), if the two lithium ions could be fully extracted. Despite significant progress, a series of critical issues—questions relating to this strategically important family of cathode materials remain open. Thus, the Li storage mechanism remains unresolved between the solid-solution and two-phase reaction of Li$_{1-x}$FeSiO$_4$ cathode in contrast to the well understood two-phase separation Li storage mechanism of LiFePO$_4$ cathode [5,6]. These differences probably come from 1) the existence of polymorphs, the atomic occupation of which can be described by different kinds of space groups (P1, P2$_1$/n, Pnn2, Pnmb, etc.) in two types of structures, namely monoclinic and orthorhombic phases [7–10]; 2) the mainly vertex-shared atomic tetrahedral coordination, which is less stable than that of the vertex/edge-shared octahedral coordination in LiFePO$_4$ olivine structure. This type of vertex-shared atomic connections can be easily changed upon Li removal and in turn perturb the Li ion migration as well; 3) the unclear phase transformations, which demonstrate rate- and particle size-dependent transformation characteristics due to the strong association between Li$^+$ and electron that can not be reliably confirmed from electrochemical cycling data [3,11,12]; and 4) the ambiguous charge compensation mechanism, which directly relates to the question of whether there is a presence of Fe$^{4+}$ ion or not for more than one Li extraction [11,13,14]. These questions remain to be resolved before the full utilization of the capacity advantage of Li$_2$FeSiO$_4$ can be materialized and further investigations are urgently needed to deepen our fundamental comprehension of the intricate structure evolution and charge compensation mechanisms.

The structural changes of Li$_2$FeSiO$_4$ cathode can be characterized by many methods, including the in-situ and/or post-mortem Raman spectroscopy, X-ray/neutron diffraction and first principles simulations. In early reports [15,16], in-situ XRD results revealed that inter-site exchange occurs between Li ions (4b site) and Fe ions (2a site) during first charge and discharge of the orthorhombic Li$_2$FeSiO$_4$ cathode material (C/25 of rate), simultaneously with the volume contraction of 1% of the unit cell from the original Li$_2$FeSiO$_4$ to the delithiated LiFeSiO$_4$ phase; additionally the inter-site exchange of Li–Fe becomes minimum on subsequent cycles [15]. Meanwhile, based on in/ex-situ X-ray diffraction measurements of partially charged samples, Dominko et al. reported that the electrochemical oxidation/reduction process of Li$_2$FeSiO$_4$ is accompanied with a fully reversible two-phase transition [17]. Follow up investigations, experimental [1,7] or theoretical [8,10,18,19], sought to further our understanding of the physical picture of Li storage mode in LFS cathode. Thus on the basis of in-situ XRD/XANES study combined with first-principles calculations, Lv et al. proposed that monoclinic Li$_2$FeSiO$_4$ undergoes two two-phase reactions when the electrode is charged to a high voltage of 4.8 V [11]. Subsequently using post-mortem synchrotron XRD analysis [12], Masese et al. demonstrated that the C/50 rate of one lithium extraction during initial cycling leads to complete transformation from monoclinic Li$_2$FeSiO$_4$ to thermodynamically stable orthorhombic LiFeSiO$_4$, concomitant with the occurrence of significant Li/Fe antisite mixing. The C/10 rate of lithium extraction and insertion, however, leads to retention of the parent monoclinic Li$_2$FeSiO$_4$ phase with little cationic mixing [12]. In a follow-up paper, Masese et al. by cycling the same (carbon-coated) LFS pristine material at elevated temperature (55 °C) found the first Li extraction to be consistent with 2-phase reaction but the second Li extraction step to have single phase behavior [14]. Aforementioned results clearly indicate a rather complex Li-ion storage behavior for LFS with apparent contradictory or missing facts or interpretations, a rather unsettling state of affairs for such an important high capacity cathode material. Summarizing, the structural evolution of LFS electrodes shows structure- [1], size- [3], rate- [3,12] and relaxation time-dependent [12] characteristics. In the meantime antisites are reported to form but their role in the structural evolution process has not been discussed.

Similarly, the charge compensation mechanism is far from being fully elucidated. Lv et al. pursued a series of investigations on the charge compensation mechanism using X-ray absorption near edge spectroscopy (XANES) [11], especially when more than one Li extraction is involved. Although two-electron transfer (Mn$^{2+}$ to Mn$^{4+}$) can be attained in polytype Li$_2$MnSiO$_4$ cathode [20], the respective electron transfer from Fe$^{2+}$ to Fe$^{4+}$ in LFS is still disputed as at the high charging voltage of 4.8 V applied, the lattice oxygen and the oxidation of organic electrolyte components could compensate the charge transfer process instead [21]. Lv et al. proposed that the Fe$^{2+}$ is oxidized to the Fe$^{4+}$ along partial extraction of the second Li$^+$ from Li$_2$FeSiO$_4$ [31]. However, these findings are directly contradictory with results by Brownrigg et al., who using in-situ X-ray absorption spectroscopy found that the valence state changes only between Fe$^{2+}$ and Fe$^{4+}$, with no evidence of Fe$^{4+}$ before the onset of electrolyte degradation at about 4.8 V [13]. This was corroborated in a latest report by Masese et al. who upon initial cycling at 55 °C and synchrotron X-ray absorption spectroscopic analysis concluded that charge compensation upon second Li extraction is accommodated via anion (O$^{2-}$) oxidation [14]. This opens a totally new view in terms of charge compensation, not solely based on cation redox chemistry, which as we demonstrate in the present study may be contributing even during the one Li extraction process.

In this study, post-mortem synchrotron XRD in combination with XANES (Fe K-edge and L-edge; Si K-edge and Oxygen K-edge) characterizations are employed to investigate further the Li-ion storage dynamics in terms of structural evolution and charge compensation by considering not only the initial and final states but various intermediate states of charge (Li$_{1-x}$FeSiO$_4$, x = 0, 0.25, 0.50, 0.75, 1.0). This is done by charging/discharging LFS at low current (C/50) to allow for structure relaxation hence unequivocal (quasi-equilibrium condition) probing of the Li storage mechanism: solid solution vs. two-phase reaction. Furthermore, cycling is not limited to the first cycle [11–14] but is extended to 10 cycles. The study involves one-Li extraction as cycling is done at room temperature [11–13] rather than elevated temperature [14] that is prone to interference from possible electrolyte decomposition side reactions [22]. For the study we employ a mixed phase (P2$_1$/n monoclinic/Pmm2 orthorhombic) metastable Li$_2$FeSiO$_4$ nanocrystalline material synthesized at 400 °C as opposed to the high temperature 600–800 °C monocrystalline LFS particles [11–14] used by others. The work provides new insight into the monoclinic to orthorhombic phase transition showing that antisite formation precedes phase transition, effectively antisites acting as nucleation sites for phase transformation initiation; phase transition is rather slow not evident in the first cycle – in contrast to previous works - but only after several cycles; structural and electrochemical data point to solid solution characteristics of Li storage in our metastable LFS as opposed to two-phase mechanism; lattice oxygen participates in charge compensation as we approach one Li extraction, i.e. at much lower charging level than previously thought having as consequence destabilization of the LFS structure. Furthermore by employing scanning transmission X-ray microscopy (STXM) in partially delithiated LFS electrode (with nominal composition Li$_{1.5}$FeSiO$_4$), we observe significant non-uniform spatial
دانلود مقاله

http://daneshyari.com/article/1283407

امکان دانلود نسخه تمام متن مقالات انگلیسی
امکان دانلود نسخه ترجمه شده مقالات
پذیرش سفارش ترجمه تخصصی
امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
دانلود فوری مقاله پس از پرداخت آنلاین
پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات