



Origin of charge compensation and its effect on the stability of oxide cathodes for Li-ion batteries: The case of orthosilicates



Peng Zhang, Su-Huai Wei*

Beijing Computational Science Research Center, Beijing 100094, China

ARTICLE INFO

Article history:

Received 5 December 2017

Received in revised form

16 March 2018

Accepted 18 March 2018

Available online 20 March 2018

Keywords:

Cathode materials

Charge compensation

Stability

Li-ion batteries

ABSTRACT

The charge-compensation mechanism and host stability of a cathode play the central role in determining its reversible capacity. Here, first-principle calculations are presented to study the charge compensation and its effect on the stability of orthosilicates, $\text{Li}_{2-x}\text{TMSiO}_4$ (TM = Fe, Mn), as the promising high-capacity cathode materials for Li-ion batteries. The charge compensation in $\text{Li}_{2-x}\text{TMSiO}_4$ upon delithiation is found to be achieved first by a combined reversible TM and oxygen redox process, originating from the dynamic response of their electronic structures to the Li ions (or electrons) removal and the associated charge transfer from the O to Fe ions, and then by the irreversible formation of O vacancy (V_O) that destroys the host stability of these materials. Whether the formation of V_O in these materials upon delithiation would occur is demonstrated to be essentially determined by the energy level of their highest occupied electronic states and can be understood by the defect charge transition mechanism which provides a quantitative way to estimate to what extent the oxygen redox could be reversibly used in a cathode that being important for the future design of high-capacity cathode materials.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past two decades, the exploration of high-capacity cathode materials for Li-ion batteries has attracted wide attentions, due to the increasing demand of modern society for powering multifunctional portable electronics, electric vehicles, as well as assembling electrical energy storage systems for the renewable energy sources [1]. In principle, the capacity of a cathode is mainly determined by the number of Li ions or the number of electrons that can be reversibly exchanged during the delithiation–lithiation process. Thus, to increase the capacity, increasing the amount of exchangeable Li ions together with the accompanying electrons in a cathode is highly desired.

Traditionally, the multi-valent TM ions in a cathode are believed to be the only active redox centers that can exchange electrons and compensate charge change during the delithiation–lithiation process. Consequently, the capacity of a cathode is thought to be solely determined by the redox capacity of the TM ions therein. Based on this traditional viewpoint, the basic requirement for developing high-capacity cathodes is to find cathode hosts with multi-electron

TM redox centers, which has promoted countless research efforts in the past twenty years [1]. However, the recent studies of Li-rich TM oxides have shed light on an alternative way to exploit the high-capacity cathode materials, that is, by utilizing the anionic redox to increase their capacities [2–11]. A cumulative cationic and anionic redox process has been demonstrated in Li-rich TM oxides, such as $\text{Li}_{2-x}\text{Rn}_y\text{Sn}_{1-y}\text{O}_3$, $\text{Li}_{1.2-x}[\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ and $\text{Li}_{1.3-x}\text{Mn}_{0.4}\text{Nb}_{0.3}\text{O}_2$, which yield much higher capacities of ~260–300 mAh/g than the traditional cathode materials [3,5,6]. Nevertheless, a critical issue for utilizing the anionic redox in a cathode is about how to avoid the formation of O vacancy (V_O) upon cycling, which would destroy its host structure and thus deteriorates the reversibility. Recent theoretical studies have identified that the pure O 2p states at the Fermi level are required to reach the anionic redox capacities, and that the relative energy of TM versus O states essentially determines the nature of the redox process among three possible mechanisms: a reversible cationic redox, a reversible anionic redox or an irreversible formation of V_O [7,8,11]. These theoretical studies provided a good phenomenological understanding of the experimental observations, however, a more quantitative estimation on the border between the reversible anionic redox and irreversible formation of V_O is still needed, if one wants to maximally utilize the anionic redox capacities in a cathode.

* Corresponding author.

E-mail address: suhuaiwei@csrc.ac.cn (S.-H. Wei).

Notably, although the recent attentions are focused on Li-rich TM oxides, polyanionic compounds may offer potential alternatives for high-capacity cathode materials. For example, the orthosilicates, $\text{Li}_{2-x}\text{TMSiO}_4$ (TM = Mn, Fe), [12–26] possess two Li ions per formula unit and thus can deliver a high capacity of ~330 mAh/g, provided both of these two Li ions are usable. So far, it has been demonstrated that an over 200 mAh/g (even ~300 mAh/g for nanosheets) capacity can be obtained in $\text{Li}_{2-x}\text{TMSiO}_4$, indicating the possible unitization of at least more than one Li ions in these materials [13–16]. However, the most critical drawback for $\text{Li}_{2-x}\text{TM-SiO}_4$ is the absence of long-term reversibility, especially for the more than one Li ions redox process. For $\text{Li}_{2-x}\text{MnSiO}_4$, it has been shown that the poor reversibility is attributed to the structural rearrangement that destroys the host structure and/or blocks the Li diffusion channels, when the Li ions are extracted; [17–22] whereas, for $\text{Li}_{2-x}\text{FeSiO}_4$, unfortunately no convincing results have been reported yet. Another important mystery of $\text{Li}_{2-x}\text{TMSiO}_4$ relates to their charge-compensation process, especially for $\text{Li}_{2-x}\text{Fe-SiO}_4$. Based on the X-ray absorption spectroscopy (XAS), Lv et al. [15,16] proposed that the charge compensation in $\text{Li}_{2-x}\text{FeSiO}_4$ upon delithiation should be achieved by the successive $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox, whereas Masese et al. [23] ascribed the charge compensation for the second Li extraction to the formation of O 2p holes rather than the oxidation of Fe^{3+} ions. More recently, Lu et al. [24] found that, despite for the second Li extraction, the lattice oxygen also participates into the charge-compensation process for the first Li extraction that appears to destabilize the cycled structure of $\text{Li}_{2-x}\text{FeSiO}_4$. These controversial arguments raise an interesting question about whether the reversible anionic redox can be also realized in polyanionic compounds to create extra capacities, for example in $\text{Li}_{2-x}\text{TMSiO}_4$, similar to what have been demonstrated in Li-rich TM oxides.

Here, we carry out the first-principle calculations to study the charge-compensation process and its effect on the stability of $\text{Li}_{2-x}\text{TMSiO}_4$. Our results illustrate that (i) when the highest occupied states (HOS) of $\text{Li}_{2-x}\text{TMSiO}_4$ is high, the charge compensation upon delithiation is achieved by a combined reversible TM and oxygen redox process, as evidenced by a significant local charge change around both the TM and O ions. We show that this cannot be simply ascribed to the covalency between the TM and O ions, as previously thought, but to the dynamic response of the electronic structure of $\text{Li}_{2-x}\text{TMSiO}_4$ to the Li ions (electrons) removal. (ii) When more Li ions (electrons) are removed and the HOS is continuously lowered upon further delithiation, the irreversible formation of V_O would occur to compensate the charge change, due to the “defect charge transition (DCT)” mechanism, which destroys the host stability and cycling reversibility of $\text{Li}_{2-x}\text{TMSiO}_4$. (iii) The TM ions in $\text{Li}_{2-x}\text{TMSiO}_4$ play the central role in modulating the HOS and thus determine the reversible capacity and cycling stability of the system.

2. Methodology

2.1. Computational details

The first-principle calculations are carried out by using the projector augmented wave (PAW) method [27] and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [28] within the density functional theory (DFT) as implemented in the VASP package [29]. The wave functions are expanded by using the plane waves up to a kinetic energy cutoff of 500 eV. Brillouin-zone integrations are approximated by using special k-point sampling of Monkhorst–Pack scheme with a k-point mesh resolution of $2\pi \times 0.03/\text{\AA}^{-1}$. The cell lattice vectors and atomic coordinates are fully

relaxed until the force on each atom is less than 0.01 eV/Å. To estimate the amount of valence charge density change around the TM and O ions upon delithiation, the Bader analysis [30] is employed.

The defect level of a V_O is calculated with respect to the valance band maximum E_{VBM} , as

$$E(q/q') = \frac{E(q') - E(q)}{q - q'} - E_{\text{VBM}} \quad (1)$$

where $E(q)$ is the total energy of the system in the charge state q [31].

The formation energy of a V_O ($\Delta H(V_O)$) in a given structure is calculated as

$$\Delta H(V_O) = E(\text{Li}_x\text{TMSiO}_4) - E(\text{Li}_x\text{TMSiO}_{4-y}) - \frac{y}{2}\mu_{\text{O}_2} \quad (2)$$

where E is the calculated total energy for a given structure and μ_{O_2} is the chemical potential of the O_2 gas at 300 K, which is estimated by

$$\begin{aligned} \mu_{\text{O}_2} = & h_{\text{O}_2}(300\text{K}, P^0) - h_{\text{O}_2}(0\text{K}, P^0) + E_{\text{O}_2}^{\text{vib}} + E_{\text{O}_2} \\ & - TS_{\text{O}_2}(300\text{K}, P^0) \end{aligned} \quad (3)$$

where P^0 is the standard pressure, h_{O_2} is the enthalpy of O_2 gas, $E_{\text{O}_2}^{\text{vib}}$ is the zero-point vibrational energy, E_{O_2} is the total energy of O_2 molecule and S_{O_2} is the entropy of O_2 gas. To correct the self-interaction error within DFT, we calibrated E_{O_2} by a comparison between the DFT calculations and experimental measurements of the formation enthalpies for several oxides [32]. The correction is -1.11 eV per O_2 that is slightly smaller than the results reported previously. For h_{O_2} and S_{O_2} , we calculate the values at $T = 0\text{K}$ and use JANAF thermochemical Tables [33] to obtain the values at $T = 300\text{K}$.

The open-circuit voltage (V_{OC}) of the oxide cathode materials is calculated by

$$V_{\text{OC}} = \frac{E_{\text{tot}}[\text{Li}_{x_2}\text{Host}] - E_{\text{tot}}[\text{Li}_{x_1}\text{Host}] - (x_2 - x_1)\mu_{\text{Li}}}{x_2 - x_1} \quad (4)$$

where x_2 and x_1 are the Li content before and after the Li extraction from the host, respectively, and μ_{Li} is the chemical potential of Li metal.

2.2. Structural model description

$\text{Li}_{2-x}\text{TMSiO}_4$ has a framework composed of a distorted hexagonal closed-packed arrangement of the O ions, with half of the tetrahedral sites occupied by the Li, TM, and Si ions. The cations can order within the tetrahedral sites in different ways, leading to a complex polymorphism. Despite some small differences, $\text{Li}_{2-x}\text{TM-SiO}_4$ polymorphs possess very similar electronic and electrochemical properties [25,26]. Thus, here we only consider the prototype $\text{Li}_{2-x}\text{TMSiO}_4$ polymorph with the $Pmn2_1$ structure, as shown in Fig. 1. The unit cell of $Pmn2_1$ $\text{Li}_{2-x}\text{TMSiO}_4$ contains $2 \times \text{Li}_{2-x}\text{TMSiO}_4$ formula unit (f.u.). For the half-delithiated compounds, LiTMSiO_4 , the Li distribution is adopted from our previous calculations, [25] where alternative Li ions are extracted to minimize the Coulomb repulsion between the remaining Li ions. Table 1 summarizes the calculated lattice constants for $\text{Li}_{2-x}\text{TMSiO}_4$, with the available experiment data. For $\text{Li}_2\text{TMSiO}_4$, we can see a good agreement between the calculated and experimentally measured values. Moreover, the calculated voltages for $\text{Li}_{2-x}\text{TMSiO}_4$ upon delithiation are given in Table 2. The good consistency between the

Download English Version:

<https://daneshyari.com/en/article/6603478>

Download Persian Version:

<https://daneshyari.com/article/6603478>

[Daneshyari.com](https://daneshyari.com)