J Mater Sci (2014) 49:8444–8448
DOI 10.1007/s10853-014-8554-z

First-principles investigation of the gas evolution from the cathodes of lithium-ion batteries during the storage test

Yongseon Kim · Dae-Yong Jeong · Seung Chul Han

Received: 14 May 2014 / Accepted: 16 August 2014 / Published online: 28 August 2014

Abstract Gas evolution related to the positive electrode of charged lithium-ion batteries during the storage test was investigated using a first-principle method. The distribution of lithium during the delithiation process was simulated based on the density functional theory calculations of the energy required to remove the lithium from the surface or bulk crystal of lithium nickel cobalt manganese oxide (NCM) and lithium cobalt oxide (LCO). Lithium coverage of the surface was smaller for LCO than NCM at a highly charged state. The energy required to form an oxygen vacancy in NCM and LCO crystal was also calculated. The results showed that LCO was more apt to emit oxygen than NCM as the delithiation percentage was increased. The results suggest that the gas-generating side reactions related to the emission of oxygen would be more significant for LCO with high voltage charging. Experimental result showed a considerable portion of the gas was generated at the initial stages of storage for NCM, whereas LCO showed slow but steady gas evolution with increasing storage time. A large amount of Li_2CO_3 or LiOH on the surface of NCM appears to cause an immediate gas-generating side reaction, whereas LCO produces slow side reaction related to the emission of oxygen from the LCO material itself.

Introduction

As mobile electronic devices become slimmer and even round-shaped, demand for design-flexible pouch-type lithium-ion batteries (LIBs) is increasing [1–3]. Gas evolution from a side reaction between the electrolyte and the positive electrode at a charged state may be the most significant problem in the industry [4–9], because pouch-type cells are not packaged in a hard metal can which is used for cylinder type cells and therefore, they are deformed easily with the gas evolution. This problem would become more and more significant as the engineers are trying to increase the voltage of battery charging for higher energy storage. Despite the significance, there are only a few reports on the gas evolution inside LIB cells, and the mechanism seems still unclear.

Previous study showed that gas evolution with the storage time at the charged state is different for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) and $LiCoO_2$ (LCO) [5]. It was found that the Ni-based layer-structure positive electrode material contained more residues of lithium compounds, such as Li_2CO_3 or LiOH, and their side reaction with electrolyte solution has been proposed to be the main cause of gas evolution at the initial stages of the storage test. Regarding LCO, it was proposed that the relatively slow but steady reaction between the material itself (i.e., $LiCoO_2$) and the electrolyte solution is the main mechanism for gas evolution [7, 10]. Nevertheless, more research is required to provide a better explanation and an effective prevention measure for gas evolution.

The aforementioned interpretation may appear unacceptable because there is a general recognition that Co-based positive electrode materials are more stable than Ni-based ones. In this study, the validity of the interpretation was examined using a first-principle method. The

---

Y. Kim · D.-Y. Jeong
Department of Materials Science and Engineering, Inha University, Incheon 402-751, Korea
e-mail: ys.kim@inha.ac.kr

S. C. Han (✉)
Department of Computer Engineering, Myongji University, Yongin, Gyeonggi-do 449-728, Korea
e-mail: bongbong@mju.ac.kr

delithiation percentage of surface and bulk crystal of NCM and LCO was estimated by density functional theory (DFT) calculations and compared. The tendency of oxygen emission from NCM or LCO crystals was estimated by calculating the energy required for the release of oxygen. On this basis, the characteristics of gas-generating side reaction for NCM and LCO were investigated to determine the proper development direction of NCM and LCO to reduce gas evolution.

Methods

Pouches containing charged cathodes and electrolyte solutions were fabricated to measure the quantity of gas generated during the storage test. CR2016 type coin half cells were fabricated using $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM, SAMSUNG SDI) and $LiCoO_2$ (LCO, Umicore) as the positive electrode material and charged to 4.45 V versus Li/Li^+ (0.1 C CC–CV). The cells were disassembled immediately after charging in a dry room with a dew point of less than −40 °C, and the positive electrodes were separated. Several pieces of the electrode containing a total of 0.3 g of the active material were collected. The pieces were rinsed several times with dimethyl carbonate (DMC), dried, and placed in a 30 × 80 mm pouch containing 0.5 g of the electrolyte solution (1 M $LiPF_6$ dissolved in a mixture of 30 vol% of ethylene carbonate, 30 vol% of DMC, and 40 vol% of ethyl methyl carbonate). The pouch was evacuated to approximately 0.1 Torr and sealed. The volume change of the pouch was measured as a function of the storage time at 60 °C to determine the level of gas evolution.

The surface and bulk of the NCM and LCO crystal were examined by first-principles DFT calculations: percentage of the remaining Li ions during the delithiation process (i.e. during battery charging) on the surface and in the bulk crystal was simulated, and the energy needed to extract an oxygen atom from the bulk crystals leaving a vacancy was calculated. The (0 0 3) and (1 0 4) surfaces, of which the surface energy was found to be the lowest from a previous study [11], were mainly considered. For the (0 0 3) surface, a Li-terminated surface with a 50 % Li-covering (i.e., Li-terminated non-polar surface) was set to be the reference surface state. Consideration of surface termination was unnecessary for the (1 0 4) surface because the surface contains oxygen, lithium, and transition metal. Therefore, there is only one kind of surface termination. The energy change with the removal of lithium one by one from the surfaces and bulk crystals was calculated, which gave an estimation of the sequence of delithiation. The energy change by the removal of oxygen from the bulk crystals was calculated at various states of the delithiation percentage to compare the tendency of oxygen emission from the NCM and LCO crystals.

The supercell composition of $Li_{12}TM_{12}O_{24}$ (TM: transition metal) was used as the calculation model. For surface calculations, vacuum slabs were inserted inside the model crystals to generate surfaces. A lithium layer was divided by the vacuum slab so that two surface planes formed by the insertion of a vacuum slab to be covered with 50 % of lithium ions for the (0 0 3) surface. This is because the (0 0 3) surface was the most stable, when it was covered by 50 % of the lithium ions by non-polar cleavage from a previous study, as mentioned previously. The energy of each compound was calculated by DFT based on the generalized gradient approximation with a correction for the self-interactions of *d* electrons (the GGA+U method: $U = 6.0$ and 5.5 eV for Ni and Co, respectively), and the projector-augmented plane wave (PAW) pseudopotentials implemented in the Vienna ab initio simulation package (VASP) with an energy cutoff of 400 eV.

Results and discussion

Figure 1 presents the accumulated amount of gas evolution measured by the volume change in the pouch containing charged electrodes and an electrolyte solution as a function of storage time at 60 °C. The pouch containing the NCM electrode showed rapid swelling at the initial stage of storage, and the swelling rate then decreased with time. In contrast, the initial volume change of the LCO pouch was small but swelling continued with increasing storage time. We tested two different products of NCM and LCO for a comparison (NCM-1, 2 and LCO-1, 2 in Fig. 1). There was a slight difference in the amount of gas evolution between NCMs or LCOs, but the overall tendency was similar for NCMs and LCOs, respectively. This confirms that there is

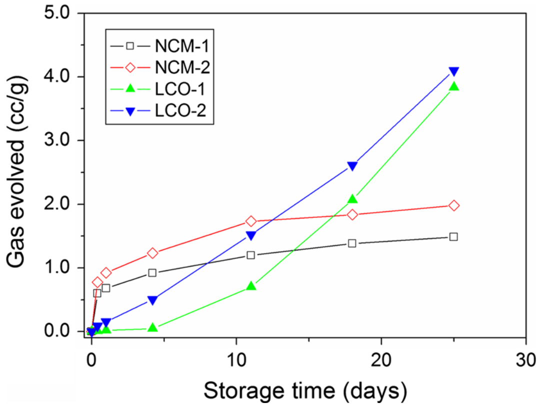

Fig. 1 Gas evolution in the pouch containing the positive electrode (NCM or LCO) at a charged state (4.45 V vs. Li/Li^+) and electrolyte solution with respect to time of the storage test at 60 °C

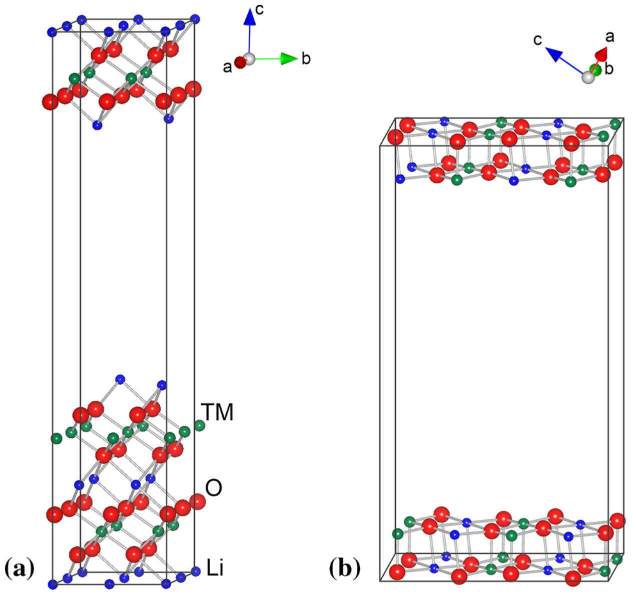

Fig. 2 Crystal model with a vacuum slab inside for an interpretation of the surface by the first-principles density functional theory calculation: **a** (0 0 3) surface with 50 % of lithium coverage and **b** (1 0 4) surface

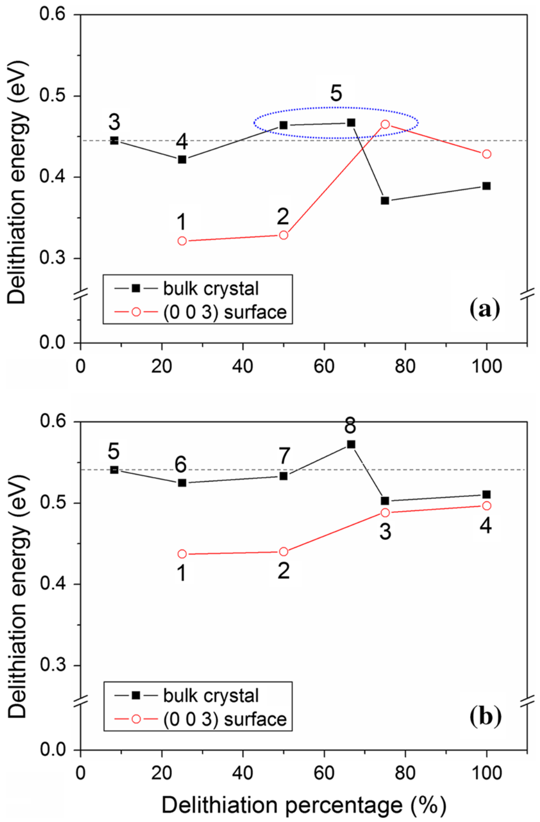

Fig. 3 Energy required to remove a lithium atom (delithiation energy) from bulk crystal or (0 0 3) surface at various delithiation percentages: **a** NCM and **b** LCO

a distinct difference in the characteristics of gas evolution between NCM and LCO. NCM at a charged state seems to generate a large amount of gas by a quick side reaction with the electrolyte. It was reported this is because the residual Li_2CO_3 or LiOH on the surface of NCM can react easily with the carbonate solvents in the electrolyte generating CO_2 as a by-product [5, 10]. This interpretation was supported by surface composition analysis, which showed that NCM contained much more Li_2CO_3 and LiOH than LCO [10].

Therefore, gas evolution at the initial stage of the storage test can be explained by a fast side reaction related to residual lithium compounds on the surface, but long-term gas evolution does not appear to be interpreted clearly (partly because most previous research focused on the firing mechanism near 200 °C rather than the steady gas evolution at a charged state). A few studies on the long-term gas evolution of LCO reported that oxygen emitted from LCO at the charged state oxidizes the solvents in the electrolyte solution [12–14]. This type of side reaction is expected to be slow and steady compared to the reaction of the residual lithium compounds on the surface, and related to the slow continuous expansion of the pouch with increasing storage time.

To examine this, the distribution of lithium ions during the delithiation process was assessed by DFT calculations: the formation energy of the supercells was obtained by DFT calculations removing lithium one by one from the surface (Fig. 2) and bulk. Figure 3 shows the energy required to remove one lithium at various delithiation states of NCM (a) and LCO (b).

For NCM, the increase in energy with the removal of one lithium from the (0 0 3) surface is smaller than that from the bulk crystal in the range of the delithiation percentage under 50 %, but became larger as the delithiation percentage was increased over 50 %. This suggests that delithiation occurs from the (0 0 3) surface first until 50 % of the surface lithium is removed, followed by delithiation from the bulk. When the delithiation percentage of the bulk reaches ∼50 %, the energy required to remove lithium from the (0 0 3) surface and from the bulk became almost identical. Therefore, the delithiation sequence may depend on the kinetic conditions. That is, the delithiation sequence is expected to follow 1–4 in Fig. 3a, and from 5, the sequence would be just a matter of kinetics or statistics. In contrast, for LCO (Fig. 3b), the energy required to remove lithium from the (0 0 3) surface is lower than that required to initiate delithiation from the bulk. Therefore, delithiation from the bulk is expected to begin after the thorough removal of lithium from the (0 0 3) surface (the sequence of 1–8 in Fig. 3b).

With a 4.45 V cutoff of the charging voltage versus Li/Li^+, approximately, 75 % and 67 % of delithiation might

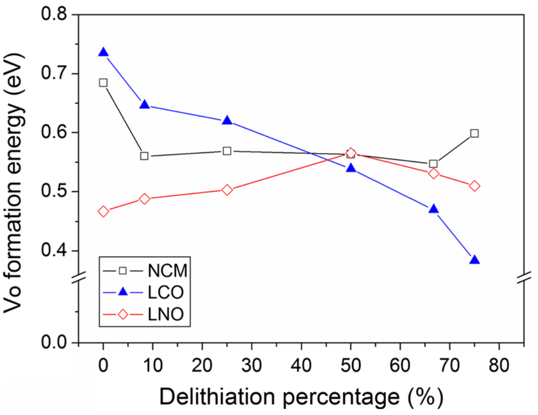

Fig. 4 Change in the energy required to form an oxygen vacancy (V_O formation energy) in the bulk crystal of NCM, LCO, and LNO as a function of delithiation percentage

be assumed for NCM and LCO, respectively. From Fig. 3, it appears that some of the lithium ions may remain on the (0 0 3) NCM surface under this charging condition, whereas the Li coverage of the (0 0 3) surface of LCO would be 0 %. Overall, the residual rate of lithium on the surface is expected to be smaller for LCO than for NCM, giving the transition metal of the LCO surface (i.e., cobalt) a higher oxidation state than those of the NCM surface. Therefore, the LCO surface is more unstable and might have a higher tendency to alleviate the instability by releasing oxygen, thus LCO would generate more gas than NCM through a side reaction induced by the release of oxygen. The calculation result for (1 0 4) surface, however, showed only a slight difference between LCO and NCM. The surface planes except for (0 0 3) have an open channel of lithium. Hence, lithium ions would move in and out continuously. Accordingly, the Li coverage of the surfaces would depend on the kinetic conditions.

The energy required to generate an oxygen vacancy in $Li_{12-x}TM_{12}O_{24}$ bulk crystal was calculated at various delithiation percentages ($x = 0, 1, 3, 6, 8, 9$), and the result for NCM and LCO is presented in Fig. 4. Strictly speaking, a calculation of the formation energy of oxygen vacancies will need to consider the after reaction of emitted oxygen and ambient oxygen partial pressure, which were assumed to be the same for NCM and LCO in the study, hence the effect of them was ignored. This simplification might be justified because a relative comparison of the tendency of oxygen vacancy formation is the main interest at this point. The energy was in the range, 0.55–0.65 eV, and did not show any interrelation with the delithiation percentage for NCM. On the other hand, for LCO, the energy was ~0.75 eV at $x = 0$, which is larger than that of NCM, and decreased consistently with increasing delithiation percentage. This suggests that oxygen vacancies tend to form in LCO at a higher delithiation percentage. LCO appears to be more able to emit oxygen than NCM under the 4.45 V charging condition.

The data of $LiNiO_2$ (LNO) are also presented in Fig. 4 for comparison. The formation energy of oxygen vacancies for LNO did not show any tendency to change with the delithiation percentage, which is similar behavior to NCM. This suggests that the tendency of oxygen vacancy formation with the delithiation percentage depends more on whether the LTMO is Co-based or Ni-based than the effect of the mixing of transition metals. This has been interpreted based on the characteristics of the density of states diagram [15]: the energy level of $Co^{3+/4+}$ is close to the O 2p levels. Therefore, the reduction of cobalt and the emission of oxygen from delithiated LCO occur.

The results can be summarized as follows. A comparison of NCM with ~75 % delithiation and LCO with ~67 % delithiation under the 4.45 V charging condition showed that LCO has less surface coverage of lithium than NCM, and the oxygen vacancy formation energy was also smaller for LCO. Therefore, LCO is more able to emit oxygen at the delithiated state and would generate more gas by a side reaction with the electrolyte solution than NCM. This mechanism of gas generation is expected to be slow but steady compared to the gas-generating reaction between Li_2CO_3 or LiOH on the surface and electrolyte, which would reflect the long-term feature of battery swelling rather than the initial stage of the storage test. On this basis, the continuous expansion of the LCO pouch presented in Fig. 1 can be explained.

As mentioned above, the maximum 75 and 67 % of the delithiation percentage was assumed for NCM and LCO, respectively, and this condition might correspond to approximately 4.45 V (vs. Li/Li^+) of charging. Considerable effort has been used to increase the charging voltage as a major strategy to achieve a higher capacity of LIBs. 4.3–4.4 V charging of LIBs (graphite anode) appears to be a realistic short-term goal, and the delithiation percentage of this study was determined considering this. The charging of LCO with a higher voltage does not seem to be desirable considering that the energy required to extract oxygen from the bulk crystal of LCO decreases consistently with increasing delithiation percentage, as presented in Fig. 4.

Conclusions

The distribution of lithium and the energy needed to form an oxygen vacancy during the delithiation process was calculated for NCM and LCO using a first-principle DFT method. The tendency of oxygen emission from the surface or bulk crystal was estimated based on the calculation results. The lithium coverage of the LCO surface was smaller at a highly charged state, and the transition metal was at a higher oxidation state compared to NCM. Therefore, the driving force to alleviate the instability by emitting oxygen would be stronger. In addition, an oxygen vacancy can be formed more easily in LCO than in NCM at the highly delithiated states. The results indicate that the gas-generating side reactions would be more significant for LCO with high voltage charging. The storage test showed that a considerable portion of the gas is generated at the initial stages for NCM, whereas LCO showed continuous gas evolution with increasing storage time. This appears to be because a relatively large amount of Li_2CO_3 or LiOH on the surface of NCM causes an immediate gas-generating side reaction with the electrolyte, whereas LCO makes slow but continuous gas generation by a side reaction related to the emission of oxygen from LCO itself. Therefore, future research will need to focus on how to reduce the residue of Li_2CO_3 or LiOH for NCM, and on the appropriate design of the crystal chemistry and structure for the suppression of oxygen emission from LCO to deal with the swelling problems of LIBs with high voltage charging.

Acknowledgements This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2014R1A1A1007800). This work was also supported by Inha University Research Grant (INHA-48578).

References

1. Dominey LA (1994) Lithium batteries. Elsevier Science B. V, Netherlands
2. van Schalkwijk W, Scrosati B (2002) Advances in lithium-ion batteries. Kluwer Academic/Plenum Publishers, New York
3. Yoshizawa H, Ohzuku T (2007) An application of lithium cobalt nickel manganese oxide to high-power and high-energy density lithium-ion batteries. J Power Sources 174:813–817
4. Kim Y (2012) Lithium nickel cobalt manganese oxide synthesized using alkali chloride flux: morphology and performance as a cathode material for lithium ion batteries. ACS Appl Mater Interfaces 4:2329–2333
5. Kim Y (2013) Investigation of the gas evolution in lithium ion batteries: effect of free lithium compounds in cathode materials. J Solid State Electrochem 17:1961–1965
6. Kumai K, Miyashiro H, Kobayashi Y, Takei K, Ishikawa R (1999) Gas generation mechanism due to electrolyte decomposition in commercial lithium-ion cell. J Power Sources 81:715–719
7. Kim Y (2013) Encapsulation of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ with a thin inorganic electrolyte film to reduce gas evolution in the application of lithium ion batteries. Phys Chem Chem Phys 15:6400–6405
8. Kong W, Li H, Huang X, Chen L (2005) Gas evolution behaviors for several cathode materials in lithium-ion batteries. J Power Sources 142:285–291
9. Holzapfel M, Würsig A, Scheifele W, Vetter J, Novák P (2007) Oxygen, hydrogen, ethylene and CO_2 development in lithium-ion batteries. J Power Sources 174:1156–1160
10. Kim Y (2013) Mechanism of gas evolution from the cathode of lithium-ion batteries at the initial stage of high-temperature storage. J Mater Sci 48:8547–8551
11. Kim Y, Lee H, Kang S (2012) First-principles and experimental investigation of the morphology of layer-structured $LiNiO_2$ and $LiCoO_2$. J Mater Chem 22:12874–12881
12. Aurbach D, Markovsky B, Shechter A, EinEli Y, Cohen H (1996) A comparative study of synthetic graphite and Li electrodes in electrolyte solutions based on ethylene carbonate dimethyl carbonate mixtures. J Electrochem Soc 143:3809–3820
13. Zhuang GV, Yang H, Ross PN, Xu K, Jow TR (2006) Lithium methyl carbonate as a reaction product of metallic lithium and dimethyl carbonate. Electrochem Solid State Lett 9:A64–A68
14. Du Pasquier A, Disma F, Bowmer T, Gozdz AS, Amatucci G, Tarascon JM (1998) Differential scanning calorimetry study of the reactivity of carbon anodes in plastic Li-ion batteries. J Electrochem Soc 145:472–477
15. Nazri G, Pistoia G (2004) Lithium batteries science and technology. Kluwer Academic Publishers, Boston