An *ab-initio* evaluation of layered oxide cathode materials for Li-ion batteries: LiMO2 (M= Mn, Fe, Co, Ni and Ni1/3Co1/3Mn1/3)

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Abstract

Theoretical investigations of cathode materials LiCoO2, LiMnO2, LiNiO2, LiFeO2, and LiMn1/3Co1/3Ni1/3O2 are performed by density functional theory (DFT), using GGA(+U). Structural properties and stability are evaluated by considering the c axis of unit-cell as a naïve indicator. Calculated force on the transition metal atoms is used as a simple indicator for cycling stability (cycle-ability). Requirement of stability in conditions of relevant atoms is proposed here as a new approach for ab-initio evaluation of cycle-ability. Comparison among the oxide cathodes show the best structural properties, stability and conductivity belong to LiMn1/3Co1/3Ni1/3O2. In terms of energy density, cycle-ability and rate-capability, LiCoO2 is the best. In contrast, relatively, LiMnO2 is not an appropriate cathode. Calculated atomic forces show that LiFeO2 suffers from low cycle-ability. LiNiO2 may suffer from ion diffusion difficulty due to its low highness of the c axis. The conclusions justify reputation of the cathodes and their relevant experimental observations.

1   Introduction

Nowadays the importance of green and efficient energy storage has increased over the past decades, largely due to concerns about global warming, lack of fossil fuel supplies, and high requirements for portable electronic devices. Lithium-ion battery (LIB) has created a new area for renewable energy storage systems as well as electronic portable devices [1]. One of today's technology challenges is modifying cathode materials to improve the LIBs efficiency to meet the ever-increasing needs for energy storage [2].

LiCoO2 (LCO) with layered structure is industrially the first and one of the most important cathode materials of LIBs. However, the expensiveness and toxicity of Co, lead researchers to use other similar transition metals (Mn, Fe, and Ni) to replace them with Co [3]. Replacing Co with Ni led to lower cost and higher capacity cathode material, but it suffers from lower structural stability, lower rate capability and more difficult synthesis in comparison with LCO [3].

LiMnO2 forms a monoclinic structure, rather than a rhombohedral, which can be converted into a hexagonal layered along the cycling path [4]. Hexagonal is the best structure for lithiation and delithiation as it has much space for lithium-ion diffusion along with the active material. Today, one of the most frequently used cathode material in this family is Li(Ni-Co-Mn)O2 composition (called NCM). The NCM which relatively contains equal amounts of three transition metals, Li(Ni1/3Mn1/3Co1/3)O2, delivers high capacity, good rate capability and can operate at high voltages [5].

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Recently, iron compounds such as LiFeO2, Fe2O3, and Fe3O4 have been considered as the active cathode and anode material for LIBs [6]. The advantage of low-cost makes iron-based compounds as promising active electrode materials for LIBs.

Density functional theory (DFT) has generated unique certainty in facility using quantum mechanics to solve interesting and challenging problems and issues in chemistry by characterizing the electrical states of materials [7-9]. DFT computational investigations open a possible land space for theoretical justification and understanding or prediction of material properties [2, 7, 10, 11]. This approach could help modifications of known cathodes, or even help to find new candidates in the future [7]. This study employs DFT calculations to evaluate LiCoO2 LiMnO2 LiNiO2 LiFeO2 and LiMn1/3Co1/3Ni1/3O2 (hereinafter called NCM) cathode materials. Structural properties, structural stability and cell voltage are reported here, and for a comprehensive comparison, electrical properties are given from our recent work [12].

2   Methodology

All calculations in this work were performed using the full- potential linear augmented plane wave (FP-LAPW) method as implemented in the Wien2K code [13] within the framework of density functional theory (DFT). The convergence of the self-consistent iterations was performed within 0.0001 Ry. Full relaxation was performed using the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA, hereinafter called GGA). The relaxation was performed in three modes (1- optimization of volume in constant ratio of a/c. 2- optimization of c/a in constant volume and 3- atomic forces minimization) as implemented by Wien2k9 code. The processes were performed many times to be sure that the structures were relaxed. To build delithiated structures, Li atoms were eliminated from the relaxed lithiated structures. For more comprehensive results and to calculate more accurate electrical properties, GGA plus an on-site Coulomb self-interaction correction potential (USIC) were applied, hereinafter called GGA+U. The U value was considered to be equal to 6 eV for Mn, Co, and Ni, and 5 eV for Fe atoms [14, 15]. The calculations were carried out as spin-polarized ferromagnetic (FM). The cathode materials of LiMO2 (M is transition metal: Mn, Co, Fe, Ni or Co1/3Mn1/3Ni1/3) with hexagonal crystal and the R-3m space group were investigated. The initial structure (structural characteristics and atomic positions) was taken from ref. [16] for LCO. The other structures were built by substitution of the transition metal with Co. For this structure, integrals were calculated over the Brillouin zone with k-points based on 9´9´1 Monkhorst–Pack (MP) mesh for R-3m structure.

More details of the methodology could be found in Electronic Supplementary Information (ESI).

3   Results

3-1- Structural properties and structural stability

In the assessed hexagonal structures, transition metal and lithium atoms are located in octahedral positions. Each unit-cell contains three unit formulas. The material structure consists of parallel plane M, O, and Li, which all of the atoms are in hexagonal configuration. This formation facilitates lithium diffusion. The planes are perpendicular to the c axis. Therefore, the c axis is important for our considerations.

Table 1 shows the calculated crystal structures for the materials in their lithiated and delithiated states and changing of the parameters after Li extraction. Axis c tolerates the maximum shrinkage, as it is expectable.

The maximum shrinkage of the cell volume (called Ω) after delithiation, 6.87% (LiNiO2), predicts a stable structure for this cathode substances during charge/discharge (structure will remain stable in less than 10% change [17]).

To inform, in tables/figures of this paper, the order of the context materials are arranged with respect to the order of the relative transition metals in the periodic table (i.e. respectively Mn, Fe, Co, and Ni).

Structural change after the extraction of Li is a criterion/indicator for structural stability. Simply, for cathode materials in *ab-initio* studies, the fewer calculated change in Ω means the more stability of the structure during charge and discharge [15, 17, 18]. On the other hand, in the case of layered oxide cathodes, change in the c axis would be important; because diffusion occurs in its perpendicular directions (the higher c value, the opener channels for diffusion). According to Table 1, the least changes of Ω were predicted for LiCo1/3Ni1/3Mn1/3O2 and the most one for LiNiO2; whereas, the most change in the c axis belongs to LiMnO2. Therefore, it is suitable to specify one appropriate indicator, to compare the structural properties of the materials with each other.

As far as considering the structural properties of these materials, there are four operating parameters. In DFT studies for Li-ion cathodes, cell volumes (3) and their changes (percentage) could simply indicate easiness of Li+ diffusion and structural stability, respectively [15, 17]. However, in such layered materials, the role of c axis should not be deniable in the Li+ diffusion and consequently the structural stability. To consider the effect of the cell parameter of c (hereinafter called "c") in the structural assessments, two approaches could be evaluated: 1- length of c and 2- hexagonality (c/a ratio, where a and c are the cell parameters). Both of the approaches are naively representing the easiness/difficulty of the Li diffusion process. Hexagonality (hereinafter called "HX") is a parameter usually considered in experimental works by using XRD patterns, especially in Li(Mn-Co-Ni)O2 materials. Increasing HX means increasing the space between planes and, as a simple result, it causes the easiness of Li atoms diffusion.

Figure 1 shows calculated cell volume (Ω), cell parameter of c (c) and hexagonality (HX) for lithiated and delithiated structures (Fig. 1 a-c), and their variations due to delithiation (Fig. 1d). As could be seen in the figure, to make a comparison between the materials, taking different indicators would result in different sorts of materials. Therefore, finally, we should prefer only one parameter as an indicator to make a comparison.

Comparing the materials according to Figure 1, Ω and c result in the same sort of the materials in delithiated structures. Considering lithiated structures, denying NCM, Ω and c cause to opposite sorts; Ω increases by increasing the atomic number of TM, whereas c decreases with it. In lithiated state, HX follows c trend. Also, in delithiated state, c and HX have similar comparison results, excepting LiMnO2. Considering the parameter alterations ($\frac{x}{x_1}$), the comparison of the materials by different parameters (Ω, c or HX) causes the same conclusion except for LiNiO2. Low hexagonality of LiNiO2 could be responsible for its potential for anti-site defects of Ni, which have been suggested for the material's low rate-capability mechanism [19]. Another proposed mechanism for the lower rate-capability of LiNiO2 (in comparison with LCO) is lower electrical conductivity [12] resulted from lithiated-delithiated junction [8]. Noteworthy, according to Figure 1d, the most stable structure is NCM, taking to account each of the parameters. For the other conclusions, we take c parameter as governing criterion, according to its importance in diffusion process. Also, between calculated values for lithiated and delithiated states, we should choose the lower one; because the lower value is always limiting a kinetic process (i.e. diffusion). Accordingly, as conclusions, NCM is the best-considered cathode material regarding both diffusion-easiness and structural-stability. The worst structure regarding diffusion easiness is LiNiO2. The lowest structural stability belongs to LiMnO2.

Table 1: Structural information calculated for lithiated (lith.) and delithiated (delith.) LiMO2

(per Angstrom), and structural changes caused by lithium excretion (in percent). In this table x is related column value and [?]x/x is equal to (x*delithiation* − x*lithiation*)/ x*lithiation* . NCM is Li(Ni1/ 3Mn1/ 3Co1/ 3)O2. Calculated cell parameter of b is equal to a.

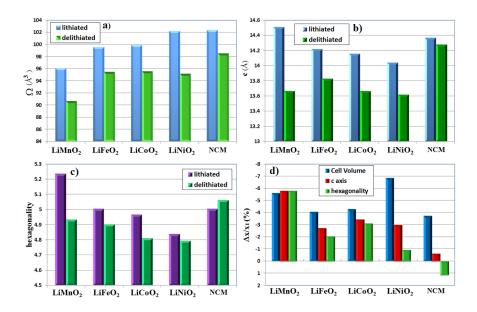| Material		a	c	Vol.
LiMnO2	lith.	2.77	14.51	96.09
	delith.	2.77	13.67	90.68
	Δx/x(%)	0	-5.79	-5.63
LiFeO2	lith.	2.84	14.22	99.59
	delith.	2.82	13.83	95.52
	Δx/x(%)	-0.7	-2.74	-4.09
LiCoO2	lith.	2.85	14.16	99.89
	delith.	2.84	13.67	95.58
	Δx/x(%)	-0.35	-3.46	-4.31
LiNiO2	lith.	2.9	14.04	102.22
	delith.	2.84	13.62	95.20
	Δx/x(%)	-2.07	-2.99	-6.87
NCM	lith.	2.87	14.37	102.37
	delith.	2.82	14.28	98.52
	Δx/x(%)	-1.74	-0.63	-3.76

Figure 1: **Calculated structural parameters of the considered materials after and before extraction of lithium. a) cell volume (Ω); b) cell parameter of c; c) hexagonality (c/a ratio) and d) their changes (%) after delithiation. Δx/x1 = (x*lithiated* − x*delithiated*) / x*lithiated*.**

3-2- Calculated forces

Table 2 shows the total amount of calculated force tolerated by the TMs in lithiated and delithiated structures (after relaxation of the structures). Changing of the force due to lithiation/delithiation could represent structural stability during discharging/charging [17]. The less change would result in the more stable TM located in its position (in the crystal) during cycling. The approach of using the calculated force has been

established for the other cathode material [17]. Here, based on our previous evaluations [17, 18], we suggest that the changing of the force could be naively interpreted to phase transition tendency under cycling. Despite, this suggestion should be investigated in more precise studies for different cases, however, it sounds obvious that in the intercalation materials, for a stable cycling, an enormous change in any parameter could risk the cycling stability. In other word, it seems obvious that in an intercalation substance, the host structure conditions should not change massively by insertion/extraction of Li atoms. We suggest that the conditions could be the force on TM or charge density around the TM etc. Hence, we use the force parameter as a simple indicator for cycle-ability. Regarding this point of view, LCO estimated to have the most stable cycling in the family (Table 2), as it is well-known. According to the table, Fe atoms in LiFeO2 would experience huge changes in the force value after (de)lithiation. Therefore, it could be considered as a cycling-unstable cathode material (low cycle-ability).

LiFeO2 has several major problems in which they prevent its presentation as a successful cathode, which could be mentioned such as a difficult synthesis process [20], low potential range [21], low cycling stability [22] and presence of several polymorphs [23]. The last parameter could be interpreted also as its low cycle-ability [17]. Despite the low cycle-ability of LiFeO2 has been observed in experimental, however, it cannot be concluded from Figure 1d (the approach of structure altering in delithiation). It shows practical importance of the noble force-related approach. Consequently, we are proposing a new approach in DFT studies of LIBs to evaluate cycle-ability. In this approach, for a good cycle-ability of the intercalation materials, the condition of the relevant atoms should not be changed enormously under delithiation.

One may tell altering of structural parameters (Fig. 1d) could also interpret to the concept of cycle-ability. Although the conception is the same, however, there is a little difference. Low structural stability could show its effect in the first cycles (Li atoms extract from the substance and are not capable to insert again), which in such a case the material should not be considered as an intercalation material. However, the instability of atomic conditions could affect the battery performance after several cycles, because the scale of the instability is the local position of the atoms.

Ταβλε 2: Τοταλ φορςε (μΡψ.αυ-1) ον τηε τρανσιτιον μεταλ ιν ΛιΜΟ2 στρυςτυρες ιν τηειρ λιτηιατεδ (λιτη.) ανδ δελιτηιατεδ (δελιτη.) στατες, ςαλςυλατεδ βψ ΓΓΑ μετηοδ. ΔΦ/Φλ ις τηε φορςε ςηανγινγ αφτερ δελιτηιατιον ανδ ιτ ις εχυαλ το (Φδελιτ. − Φλιτη.)/Φλιτ.

Material		F (mRy.au-1)	ΔF/Fl (%)
LiMnO2	lith.	1.441	
	delith.	0.514	-64
LiFeO2	lith.	1.871	
	delith.	11.396	509
LiCoO2	lith.	1.887	
	delith.	1.401	25
LiNiO2	lith.	2.052	
	delith.	1.396	31
NCM	lith.	Co=9.566 Mn=6.794 Ni=1.521	
	delith.	Co=15.048 Mn=3.881 Ni=0.671	Co= 57 Mn= 42 Ni= 56

3-3- Cell voltages

Calculated theoretical voltages (Vth) by GGA and GGA+U of the cathode materials are shown in Figure 2. According to the data, it could be derived that in both calculation methods, LiMnO2 and then NCM

would deliver the lowest voltage, respectively. In GGA+U method, the maximum voltage belongs to LiFeO2 gaining 4 V, and in GGA one, LiCoO2 has got the highest voltage (3.36 V). In experimental works, nominal voltage of LiMnO2, LiFeO2, LiCoO2, LiNiO2 and NCM was 3.7 [24], 3.6 [25], 3.6 [24], 3.8 [24] and 3.6 V [24], respectively. According to the experimental results, values obtained by GGA+U seem the better estimations.
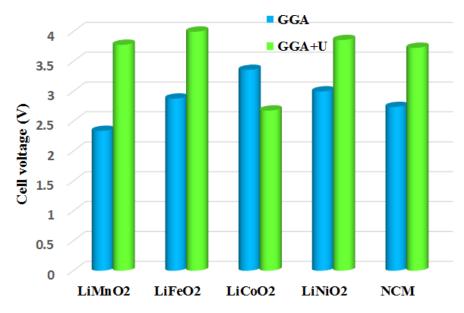

Figure 2: Theoretical cell voltages calculated by GGA and GGA+U methods.

3-4- Electrical properties

The electrical properties of the materials were considered in details in our other work, using density of states (DOS) diagrams [12]. Therefore, here, we avoid duplicating evaluations and discussions and use our previous conclusions [12], just to complete the comparison between the materials.

It was concluded that NCM, LiFeO2, LiCoO2, LiMnO2, and LiNiO2 exhibited the best to the worst electron conductivity, as far as the extrinsic-like band-gap (ELBG) would be considered. Delithiation usually caused better electron conductivity.

Considering intrinsic-like band gaps (ILBGs), the best (worst) conductivity of lithiated materials belonged to NCM and LiFeO2 and the worst belonged to LiMnO2 and LiNiO2. ILBGs of delithiated structures showed that the best (worst) obtained conductivity belonged to FeO2 (MnO2).

Rate-capability was compared quantitatively by aligning Fermi levels and evaluating difference between valance band maximum (VBM) in DOS diagrams of lithiated and delithiated materials. For rate-capability, sort of the best to the worst materials were LiCoO2, LiFeO2-NCM, LiNiO2 and LiMnO2 [12].

4   Conclusion

In this study, LiMO2 (M= Mn, Fe, Co, Ni and Mn1/ 3Co1/ 3Ni1/ 3) cathodes of lithium-ion batteries were surveyed using DFT calculations. Structural parameters, structural, cycle-ability, cell voltage and electrical properties of these materials were assessed.

The calculations showed that the best cathode among the investigated materials in terms of electrical conductivity, rate capability, structural stability and cycle-ability (so lifetime of the battery) were NCM and LCO. The theoretical properties of NCM and LCO were favorable as observed in experimental. LiMnO2 (with Hexagonal structure) was not relatively recognized as a suitable cathode material due to the lack of proper structural stability, cell voltage, electron conductivity (especially in its delithiated state) and rate capability.

Here, we suggest that an enormous change in conditions of atoms in the structure could interpret as low cycle-ability. Based on this new approach, LiFeO2 indicated as a structurally unstable cathode material under cycling, due to dramatically increasing of force on Fe after delithiation; however, it may deliver the highest voltage in the considered materials. Also, LiNiO2 suffers from lower structural stability, and rate capability (due to its electrical properties and diffusion easiness) in comparison with LCO and NCM. The conclusions justify the reputation of the cathode materials (NCM and LCO are more famous than the others).

5   Conflicts of interest

The authors declare no conflict of interest.

6   Acknowledgments

7   References

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