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Ab initio calculations of $Li_2(Co, Mn)O_8$ solid solutions for rechargeable batteries

Roberts Eglitis
Institute of Solid State Physics, University of Latvia,
8 Kengaraga str., Riga LV1063, Latvia
rieglitis@gmail.com

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Current commercially available rechargeable Li-ion batteries, for example $LiCoO_2$, are working mostly in the 4 V regime. One often suggested possibility to improve the effectivity of Li-ion batteries are the creation of the 5 V cathode materials. We performed quantum mechanical calculations on the average battery voltage for the $Li_2Co_xMn_{4-x}O_8$ (x = 0, 1, 2, 3 and 4) cathode materials by means of the WIEN2k computer program package. The calculated average battery voltages for x = 0, 1, 2, 3 and 4 are equal to 3.95, 5, 4.47, 4.19 and 3.99 V. Our *ab initio* calculation results are compared with the available experimental data for x = 0, 1, 2 and 4 which are equal to 4, 5, 5 and 4 V. Thereby, for the $Li_2Co_1Mn_3O_8$ battery cathode material, our calculated average battery voltage around 5 V is in perfect agreement with the experimentally available battery voltage value of 5 Volt. Nevertheless, our calculated average battery voltage is underestimated (4.47 V) for the $Li_2Co_2Mn_2O_8$ cathode material, which also experimentally exhibits the 5 V voltage.

Keywords: 5 V rechargeable Li-ion battery; $Li_2Co_1Mn_3O_8$ cathode material; average voltage.

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1. Introduction

It is worth noting, that the lithium-ion battery belongs to the family of rechargeable batteries. Along with numerous applications in consumer electronics, lithium-ion batteries are also very popular for military and aerospace applications. The battery business of the 21st century has exploded into a multi-billion dollar enterprise. The current market leader, the lithium-ion battery, is a promising advanced rechargeable battery. Nowadays, consumer electronics widely use lithium-ion batteries containing $LiCoO_2$ cathode, which unfortunately contains some safety problems. The $LiCoO_2$ usefulness as an intercalation electrode was discovered in 1980 by

Goodenough's group in Oxford.[1] The first rechargeable Li-ion commercial battery, employing $LiCoO_2$ as a cathode material, was put into market by Sony in 1989.[2,3] It is well known that the experimentally measured $LiCoO_2$ average intercalation voltage is equal to 4.0–4.1 V.[4]

It is interesting to not that experiments in battery area require great amount of manpower and time. At least 1000 cycles or even more should be performed using commercially interesting cells while exhibiting nearly constant performance. Due to rapid development of new calculation methods as well as explosive improvement of computers, the *ab initio* quantum chemistry nowadays can predict chemical and physical properties of novel materials. It is definitely worth to use this tool for theoretical prediction of favorable new battery cathode materials, thereby saving time and avoiding needless experimentation and focusing research work only on prospective materials that promise a high probability of success.

Theory of *ab initio* calculations for average battery voltage was developed by Ceder and his co-workers.[5–10] Ceder *et al.* calculated the average intercalation voltage of large amount of battery cathode materials and found it to be always considerably below 5 V. For example, the calculated intercalation voltage for $LiCoO_2$ by Ceder *et al.* was 3.75 V,[9] in a good agreement with the experimentally measured $LiCoO_2$ average intercalation voltage around 4.0–4.1 V.[4] One logical and frequently discussed direction how to improve the battery performance is to design the Li-ion rechargeable battery with 5 V cathode material.

Indeed, soon experimentally the first in the world single-cell lithium battery system which operate over 5 V for a large part of discharge, using a novel cathode material $Li_2Co_1Mn_3O_8$, was reported by Kawai *et al.* in 1998.[11,12] Discharge performance was limited to ca. 40 mAh g^{-1} at 5 V.[12] Nevertheless, this clearly shows the possibility to develop industrially important high voltage 5 V rechargeable Li-ion batteries. It is important to notice, that the 5 V battery cathode material was also confirmed theoretically by Eglitis and Borstel in 2005[13] using $Li_2Co_1Mn_3O_8$ as a high-voltage battery cathode material. Finally, it is worth to notice that the research progress of the 5 V cathode materials for advanced Li-ion batteries has been reported in recent years in Refs. 14–17 as well as highly efficient battery anode materials and associated *ab initio* simulations were reported in Refs. 18 and 19.

2. Technical Calculation Details

2.1. *Spinel type structure for battery cathode material*

As a starting point of performed *ab initio* average battery voltage calculations, the classical spinel structure for $LiMn_2O_4$ is plotted in Fig. 1. Above mentioned spinel structure belongs to the space group Fd3-m (No. 227). As we can see from Fig. 1, in our calculated structure, 32 oxide ions form a face centered cubic lattice.[20] Lithium ions occupy eight tetrahedral sites, whereas manganese ions 16 octahedral sites between 32 oxide anions. Fractional coordinates in space group Fd3-m, used in our calculations, are listed in Table 1 and schematically plotted in Fig. 1.

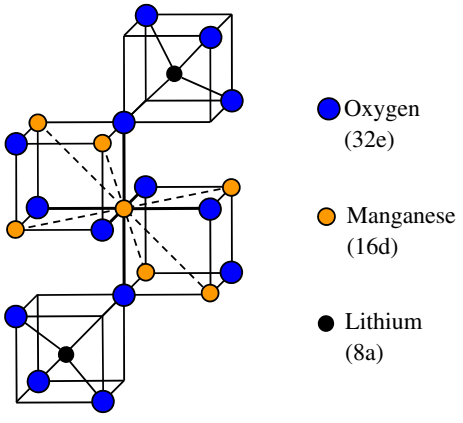

Fig. 1. (Color online) Part of the unit cell of $LiMn_2O_4$ cubic spinel.

Table 1. Coordinates of equivalent positions of atoms in the $LiMn_2O_4$ spinel for Li, Mn and O atoms.

Atom	Site	Equivalent positions	
Li	8*a*	(0, 0, 0)	(0.25, 0.25, 0.25)
Mn	16*d*	(0.625,0.625,0.625)	(0.625,0.875,0.875)
		(0.875,0.625,0.875)	(0.875,0.875,0.625)
O	32*e*	(u, u, u)	$(0.25-u,0.25-u,0.25-u)$
		$(u, -u, -u)$	$(0.25-u,0.25+u,0.25+u)$
		$(-u, u, -u)$	$(0.25+u,0.25-u,0.25+u)$
		$(-u, -u, u)$	$(0.25+u,0.25+u,0.25-u)$

The experimental value of the internal parameter u for the perfect $LiMn_2O_4$ crystal is equal to 0.390.[21]

2.2. *Theory of the average battery voltage*

As it was suggested almost 20 years ago by Ceder *et al.*,[5,9] the open circuit voltage (OCV) is possible to calculate by means of Eq. (1). The OCV is equal to the chemical potential difference for Li in the anode and cathode (as an example using the composition LiM_2O_4):

$$V(x) = \frac{\mu_{\mathrm{Li}}^{\mathrm{Anode}} - \mu_{\mathrm{Li}}^{\mathrm{Cathode}}}{zF}. \tag{1}$$

F is the Faraday constant. In the current study M = Mn or Co. Charge z is connected with Li movement from the electrode (for Li case, $z = 1$). The methology for calculation of $\mu_{\mathrm{Li}}^{\mathrm{Cathode}}(x)$ exists,[22,23] but unfortunately its computation is very time consuming. Taking into account the above mentioned, the average OCV was detected over a full charge/discharge cycle. In other words, the OCV was determined by integrating Eq. (1) between compositions M_2O_4 and LiM_2O_4. As a result it was

considered that the classical Nernst equation for the average OCV:

$$\bar{V}(x) = \frac{-\Delta G_r}{(x_2 - x_1)F}, \tag{2}$$

where ΔG_r is the change for the Gibbs free energy. The classical equation for the Gibbs free energy is written as follows:

$$\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r, \tag{3}$$

where ΔE_r is the change in internal energy. P is the pressure and ΔV_r is the volume change. T is the temperature, and, lastly, ΔS_r is the change in the entropy. In Eq. (3), the term $P\Delta V_r$ is of the order of 10^{-5} eV, and thereby we can neglect this negligibly small term in our *ab initio* calculations. Just opposite, the term ΔE_r is of the order of 3–4 eV per molecule. Lastly, the term $T\Delta S_r$ is of the order of the thermal energy.[5] Thereby it is also considerably smaller than ΔE_r. Taking into account the above mentioned, we can make conclusion, that the changes in the Gibbs free energy as well as the changes in the internal energy are approximately the same:

$$\Delta G_r \approx \Delta E_r. \tag{4}$$

It means, that in our case, ΔG_r is the Gibbs free energy for the following reaction:

$$M_2O_4(\text{cath}) + \text{Li(anode)} \rightarrow \text{LiM}_2O_4(\text{cath}). \tag{5}$$

In this contribution, voltage was detected using a solid solution $Li_2Co_xMn_{4-x}O_8$ (x = 0, 1, 2, 3, 4) as a cathode. The average voltage for $Li_2Co_xMn_{4-x}O_8$ was detected as the total energy changes for three compounds. The above discussed case ($x = 0$) is calculated as the total energy difference in Eq. (6):

$$Mn_2O_4 + \text{Li} \rightarrow \text{LiMn}_2O_4. \tag{6}$$

The average voltage (x = 1, 2, 3 and 4) of the $Li_2Co_xMn_{4-x}O_8$ can be calculated using Eq. (7) as the difference of total energies of three chemical compounds:

$$\text{LiCo}_xMn_{4-x}O_8 + \text{Li} \rightarrow Li_2Co_xMn_{4-x}O_8. \tag{7}$$

2.3. *FP-LAPW ab initio battery calculation details*

We performed our calculations by means of the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. We employed the WIEN2k computer code[24] for spin polarized mixtures of $Li_2Mn_4O_8$ and $Li_2Co_4O_8$. Exchange and correlation effects were described within the Generalized Gradient Approximation (GGA).[25] All our calculations for the battery cathode materials $Li_2Co_xMn_{4-x}O_8$ (x = 0, 1, 2, 3, 4) were spin polarized calculations. The Brillouin zone integration over 125 k points were performed. We used muffin tin radius of 1.9 a.u. for Mn and Co as well as 1.7 a.u. for Li and O. It is worth to notice, that ideal $Li_2Mn_4O_8$ has a cubic lattice. Symmetry group is Fd3-m (no. 227, spinel-type). $Li_2Mn_4O_8$ contains 14 atoms per

primitive cell and it is antiferromagnetic. The antiferromagnetic and ferromagnetic $LiMn_2O_4$ total energy difference is negligible, namely around 0.02 eV.[26] In our calculations, we used $1 \times 1 \times 1$ times extended $Li_2Co_xMn_{4-x}O_8$ supercells ($x = 0$, 1, 2, 3, 4) containing 14 atoms. We always fixed our supercells in a cubic shape. Thereby, we have neglected any relaxation of the lattice around the Li vacancy, for example, in the $Li_1Co_1Mn_3O_8$ system containing 13 atoms. We calculated the average voltage for the $Li_2Co_1Mn_3O_8$ cathode from Eq. (7).

3. Our Main Battery Calculation Results and Their Experimental Confirmations

As a starting point of our numerical *ab initio* calculations, from a minimum of total energies, we got the bulk lattice constant for $Li_2Mn_4O_8$. The calculated lattice constant a for $Li_2Mn_4O_8$ is 15.51 a.u., and thereby it is an almost perfect coincidence with the experimentally measured lattice constant of 15.57 a.u.[21] We calculated also the lattice constant for $Li_2Co_4O_8$ equal to 15.22 a.u., thereby it is also in almost perfect agreement with the experimental lattice constant of 15.10–15.12 a.u. for the $Li_{1-x}Co_2O_{4-\delta}$ as described in Ref. 27. Assuming the spinel structure also for the all solid solution $Li_2Co_xMn_{4-x}O_8$ ($x = 0$, 1, 2, 3, 4) and applying the Vegard rule, for example, for $Li_2Co_1Mn_3O_8$ we find the lattice constant of 15.44 a.u. For the $Li_2Mn_4O_8$, our calculated internal parameter $u = 0.388$, again is in almost perfect coincidence with the experimentally detected internal parameter value of $u = 0.390$.[21] Finally, our calculated internal parameter u for $Li_2Co_4O_8$ is equal to 0.389. It means that according to our calculation, there is practically no variation of the internal parameter u in the Mn–Co series. We used the theoretically calculated lattice constant a and internal parameter u in the following battery average voltage calculations.

As a next step, we calculated the cathode voltage for all concentrations ($x = 0$, 1, 2, 3, 4) of the solid solution $Li_2Co_xMn_{4-x}O_8$ (Fig. 2). Our computed voltage for $Li_2Mn_4O_8$ cathode case is equal to 3.95 V (Table 2). Experimentally, the removal of Li from $LiMn_2O_4$ cathode material in the cubic spinel structure happens via a two-step reaction around 4 V. Two plateaus can be observed in the charge line, separated by 100–150 mV.[28,29]

The average battery voltage for the $Li_2Co_1Mn_3O_8$ cathode material was computed by us using Eq. (7) as a total energy difference. It is worth to notice, that we check that the computed average battery voltage is stable against variation of the coordinates of Co and Mn atoms and a position of the Li vacancy in the $Li_2Co_1Mn_3O_8$ matrix. Namely, we computed all eight (4×2) possible geometrical configurations. The average battery cathode voltage, as computed from Eq. (7) for $Li_2Co_1Mn_3O_8$ cathode material all eight possible geometrical configurations are equal to: 4.90, 4.97, 4.99, 4.99, 5.00, 5.02, 5.02 and 5.05 V. As we can see, the average $Li_2Co_1Mn_3O_8$ battery cathode voltage for different configurations are in the range from 4.90 V to 5.05 V, or in another words always close to 5 V.

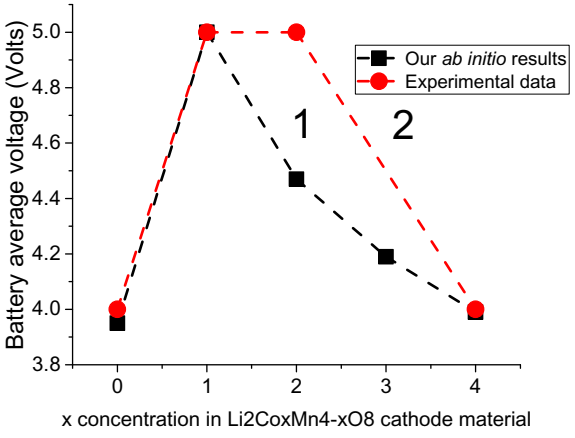

Fig. 2. (Color online) Our FP-LAPW calculated average battery voltage for solid solution $Li_2Co_xMn_{4-x}O_8$ employed as a Li-ion battery cathode material (line 1). Relevant experimentally measured battery voltages are listed for a comparison purposes (line 2).

Table 2. Our FP-LAPW calculated average battery voltages (in Volts) for a series of a cathode materials $Li_2Co_xMn_{4-x}O_8$ (x = 0, 1, 2, 3, 4). The experimental values are listed for comparison purposes.

Cathode material	FP-LAPW calculated average voltage	Experiment
$LiMn_2O_4$	3.95	4[28,29]
$Li_2Co_1Mn_3O_8$	5	5[11,12]
		5[30,31]
		5[32]
$Li_2Co_2Mn_2O_8$	4.47	5[33–35]
		5[36]
		5[37]
$Li_2Co_3Mn_1O_8$	4.19	
$LiCo_2O_4$	3.99	4[38]

The experimental result dealing with 5 V battery cathode material reported by Kawai *et al.*[11,12] was, for example, later confirmed experimentally also by Yoon *et al.*,[30] who synthesized the $LiM_{0.5}Mn_{1.5}O_4$ (M = Ni, Co, Cr) cathode material. According to the reported results, $LiM_{0.5}Mn_{1.5}O_4$ exhibited a discharge curve starting at 5 V.[30,31] It is worth to notice, that nowadays, most of the scientifical work dealing with spinel-type battery cathode materials has been concentrated on mixed manganese-oxide-based materials $Li_xM_yMn_{2-y}O_4$ (M = Ni, Co, Fe, Cr). Between these materials are a considerable amount of 4.8 or even 5 V cathodes.[32] Additionally, the recent experimental data for potential 5 V batteries are published in Refs. 33–35. Also Kawai *et al.*[36] experimentally confirmed that $LiCoMnO_4$ shows a discharge capacity of 95 mAh g^{-1} on a plateau centered at 5.0 V.[36] Finally, Huang *et al.*[37] synthesized the 5 V spinel material $LiCoMnO_4$.

Our calculated average battery voltage for Li_2Co_3Mn1O8 cathode material is equal to 4.19 V (Table 2). To the best of our knowledge, we do not know any experimental data dealing with the battery voltage for $Li_2Co_3Mn_1O_8$ cathode material. Finally, our calculated average battery voltage for $LiCo_2O_4$ in the cubic spinel structure is 3.99 V. It is very close to the experimentally measured $LiCo_2O_4$ battery cathode material voltage in the cubic spinel structure, which is well known in the battery field, and are around 4 V.[38]

4. Conclusions

Due to explosive increase of computational power as well as development of forefront numerical methods, nowadays it is already possible to design new materials and devices for industrial use on paper, thereby saving the time and money for very expensive and time consuming experimental work. Currently, in the market, available Li-ion batteries are working mostly in the 4 V regime. *Ab initio* average voltage calculations for 4 V batteries have been performed by Ceder and his co-workers.[5–7]

Our calculated average battery voltage for $LiMn_2O_4$ in the cubic spinel structure (3.95 V) is almost in a perfect agreement with the available experimental data around 4 V.[25,26] The same is true also for our *ab initio* calculations performed for $LiCo_2O_4$ in the cubic spinel structure (3.99 V), which also is in a perfect coincidence with the available experimental data around 4 V.[35]

Next, our calculated average battery cathode voltage for $Li_2Co_2Mn_2O_8$ is equal to 4.47 V (Table 2), which is around half Volt lower than the experimentally measured battery cathode voltage for $LiCoMnO_4$ in the cubic spinel structure around 5 V.[33–37] Our calculated average battery cathode voltage for $Li_2Co_3Mn_1O_8$ is equal to 4.19 V. This is pure theoretical prediction, since to the best of our knowledge, we do not know any existing experimental data dealing with the $Li_2Co_3Mn_1O_8$ battery cathode material voltage measurements (Table 2). Last, but not least, our calculated average battery voltage, using as a rechargeable Li-ion battery cathode material $Li_2Co_1Mn_3O_8$ is equal to 5 V (Fig. 2). This our calculated 5 V average battery voltage for the $Li_2Co_1Mn_3O_8$ cathode is numerous times confirmed also experimentally.[11,12,30–32]

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