

Theoretical prediction of the 5 V rechargeable Li ion battery using $\text{Li}_2\text{CoMn}_3\text{O}_8$ as a cathode

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Abstract

Due to the rapid development of computers and cutting edge research methods, it is now possible to use a quantum mechanical electronic structure theory of solids to obtain, completely from first principles, the average voltage of a battery based on intercalation reaction energetics. The results of *ab initio* calculations by means of the full potential linearized augmented plane wave (FP-LAPW) method, using the computer code WIEN2k, for spin-polarized mixtures of $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ ($x=0, 1, 2, 3$ and 4), treating exchange and correlation effects within the generalized gradient approximation (GGA), are presented. The calculated average battery voltage for $\text{Li}_2\text{CoMn}_3\text{O}_8$ cathode material is around 5 volts. The *ab initio* calculation result for a 5 V average battery voltage perfectly describes recently experimentally-synthesized $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ battery cathode material, which showed a discharge plateau starting at around 5 V. The calculated average battery voltages for other x values in the mixture $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ ($x=0, 2, 3$ and 4) (3.95 V; 4.47 V; 4.19 V and 3.99 V) are considerably below 5 V.

Keywords: *Ab initio* calculations, 5 V Li ion battery, average voltage, $\text{Li}_2\text{CoMn}_3\text{O}_8$ cathode

Introduction

After the discovery by Mizushima *et al* [1] that Li ions can be removed and re-intercalated in LiCoO_2 , a considerable amount of research has been carried out on this material, motivated by its application as an intercalation electrode in rechargeable Li-ion batteries [2, 3]. Used in rechargeable systems, cells constructed from easily oxidized, lightweight lithium typically operate at higher voltages and provide more electricity than non-lithium batteries of equal size and weight. These features stem from lithium's properties; for example, lithium's low density and high standard reduction potential.

The predictive power of *ab initio* quantum electronic structure simulations due to the improved performance of computers, as well as the development of advanced computational methods, allows for the design on paper of new materials for high technology applications. A good example is the eighteen-year-old prediction from first principles of the average battery voltage for a series of cathode materials by Ceder *et al* and other groups [2–7]. According to their calculations, the currently available lithium batteries are

operating mainly in the 4 V regime. For example, the average voltage for LiCoO_2 , calculated by Ceder *et al* [2–4], is 3.75 V and, as is well known, the layered LiCoO_2 battery has been the most widely used commercial lithium ion battery in the world since the commercialization of the lithium ion battery in 1990, due to its reasonably high capacity, long cycle life, and good processibility. The batteries for which the voltage was calculated theoretically by Ceder *et al* [2–4] operate mostly in the 4 V regime. For example, the average intercalation voltage for Li in various LiMO_2 compounds in the $\alpha\text{-NaFeO}_2$ structure, as calculated with the pseudopotential method by Ceder and his co-workers, are the following: LiTiO_2 (2.14 V); LiVO_2 (2.81 V); LiMnO_2 (3.13 V); LiCoO_2 (3.75 V); LiNiO_2 (2.92 V); LiCuO_2 (3.66 V); LiZnO_2 (4.41 V); LiAlO_2 (4.7 V) [2–4].

Two ways of improving the battery are frequently discussed; either the discharge capacity of the cathode could be increased or the working potential of the cathode materials could be increased [8]. It is well known that in the spinel LiMn_2O_4 structure the maximum theoretical discharge capacity is 148 mAh g^{-1} and, experimentally, its initial discharge

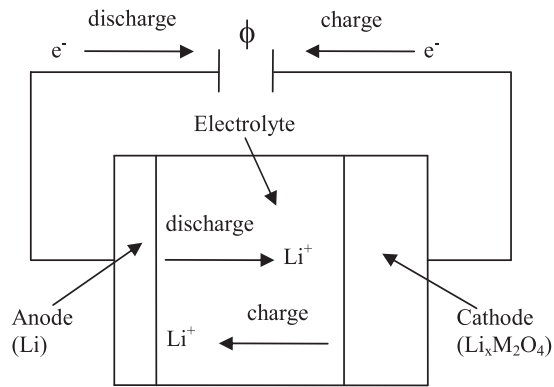


Figure 1. Sketch of a rechargeable Li ion battery. When the battery discharges Li is intercalated into the cathode compound. Upon charging the Li ions are removed from the cathode.

capacity in the 4 V range is about 130 mAh g^{-1} , with a large capacity fading upon cycling [9–11]. In 1998 Kawai *et al* [12, 13] launched the first single-cell lithium battery system to operate over 5 V for a significant period of discharge, by incorporating a novel cathode material, $\text{Li}_2\text{CoMn}_3\text{O}_8$. The battery discharge performance was limited to ca. 40 mAh g^{-1} at 5 V [12, 13], but nevertheless this opens up the possibilities for developing practical 5 V Li ion batteries. Recently, it has been reported, independently by several groups, that the high voltage spinel oxides with the composition $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Ni}, \text{Cr}, \text{Co}, \text{Cu}$, or any other transition metal element) have outstanding properties, such as, for example, high potential, high energy density, and high rate capability [14–16]. Recently, in 2007, Yoon *et al* [14] synthesized the $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{M}=\text{Ni}, \text{Co}, \text{Cr}$) cathode materials by the solid state route. The authors found that these cathode materials showed a discharge plateau starting at around 5 volt [14].

Calculation of the battery's average voltage

As was discovered eighteen years ago by Ceder and his co-workers [4], the open cell voltage (OCV) for a Li ion battery (see figure 1) is proportional to the chemical potential difference for Li in the anode and in the cathode (with composition, for example, LiM_2O_4),

$$V(x) = -\frac{\mu_{\text{Li}}^{\text{Cathode}} - \mu_{\text{Li}}^{\text{Anode}}}{zF} \quad (1)$$

where F is the Faraday constant, in my case $\text{M}=\text{Mn}$ or Co , and z is the charge associated with Li displacement from the electrode (for Li, $z=1$). Although the methodology for calculating $\mu_{\text{Li}}^{\text{Cathode}}(x)$ exists [17, 18], its computation is time consuming. Therefore, rather than calculate the OCV as a function of x , the average OCV was determined over a full charge/discharge cycle simply by integrating equation (1) between compositions M_2O_4 and LiM_2O_4 , and the classical

Nernst equation for the average OCV was obtained [4];

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

where ΔG_r is the Gibbs free energy. The well known expression for the Gibbs free energy is the following:

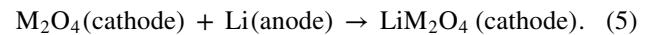
$$\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r \quad (3)$$

where ΔG_r is the change in the Gibbs free energy, ΔE_r is the change in internal energy, P is the pressure, ΔV_r is the volume change, T is the temperature, and, finally, ΔS_r is the entropy change.

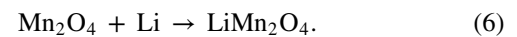
Here the term $P\Delta V_r$ is of the order of 10^{-5} electron volts. In contrast ΔE_r is of the order of 3–4 eV per molecule. Finally, the term $T\Delta S_r$ is of the order of the thermal energy which is also much smaller than ΔE_r . So, it was possible to conclude that the changes in the Gibbs free energy are approximately equal to the changes in internal energy.

$$\Delta G_r \approx \Delta E_r. \quad (4)$$

Consequently, in the case under study, ΔG_r is the Gibbs free energy for the following reaction:



The average battery voltage was calculated using as a battery cathode material, the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ ($x=0, 1, 2, 3, 4$). The average battery voltage for different cases ($x=0, 1, 2, 3, 4$) was calculated as the total energy changes in the following reactions. For example, the case with ($x=0$) corresponds to the total energy difference in equation (6):



The average battery voltage for ($x=1, 2, 3$ and 4) concentrations at the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ can be calculated from the general equation (7) as the difference between the calculated total energies using the WIEN2k computer code,



Calculation details

Ab initio calculations in the framework of the current paper, for the battery cathode materials, have been performed in the LiMn_2O_4 spinel structure (space-group: $\text{Fd} - 3\text{m}$), consisting of a cubic close-packed (ccp) array of oxygen ions, which occupy the 32e position. Mn ions are located in the 16d site, and Li ions in the 8a site. The Mn ions have an octahedral coordination to the oxygens, and the MnO_6 octahedra share edges in a three-dimensional host for the Li guest ions (see figure 2). The 8a tetrahedral site is located furthest away from the 16d site of all the interstitial tetrahedra (8a, 8b and 48f) and octahedra (16c). Each of the 8a tetrahedron faces is shared with an adjacent, vacant 16c site. Such a combination of structural features in the cubic stoichiometric spinel compound constitutes a very stable structure. For example, the

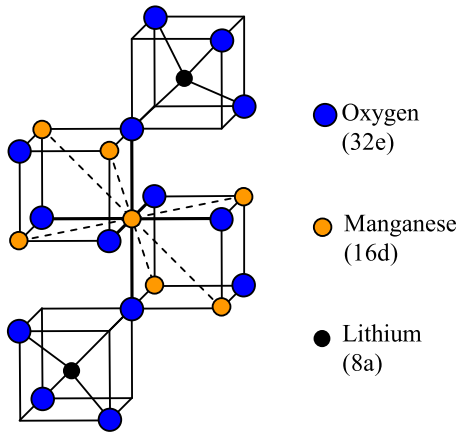


Figure 2. Part of the cubic spinel $Fd-3m$ unit cell of LiMn_2O_4 showing the local structure around. Octahedrally coordinated manganese in an ideal spinel lattice. Mn-O bonds are represented by heavy solid lines; linear chains of manganese ions in neighbouring edge-sharing octahedra are indicated by dashed lines.

current *ab initio* calculations for ideal $\text{Li}_2\text{Mn}_4\text{O}_8$ with a cubic lattice, with symmetry group $Fd-3m$ (number 227, spinel-type) were performed using the primitive cell containing 14 atoms and the smallest possible lattice extension ($1 \times 1 \times 1$). The calculations for solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ with different x ($x=1, 2, 3, 4$) were performed using the same sized primitive cell containing 14 atoms, and replacing consequently four Mn atoms by 1, 2, 3 or 4 Co atoms.

All numerical *ab initio* calculations were performed by means of the full potential linearized augmented plane wave (FP-LAPW) computer code, WIEN2k [19], for spin polarized mixtures of $\text{Li}_2\text{Mn}_4\text{O}_8$ and $\text{Li}_2\text{Co}_4\text{O}_8$, including exchange and correlation effects within the generalized gradient approximation (GGA). All *ab initio* calculations for battery cathode materials were spin polarized. Brillouin zone integration over 125 k points and muffin tin radius of 1.9 a.u. for Mn and Co atoms and 1.7 a.u. for Li and O atoms, respectively, were used.

Main calculation results

Using the total energy results calculated using the WIEN2k computer code, the crystal lattice constant a for the ideal $\text{Li}_2\text{Mn}_4\text{O}_8$ was found to be 15.51 a.u., which is in excellent agreement with the experimental data of 15.57 a.u. [20]. According to the current calculations for the hypothetical ideal $\text{Li}_2\text{Co}_4\text{O}_8$ spinel a theoretical lattice constant a is equal to 15.22 a.u., which is in quite good agreement with the experimental data of 15.10–15.12 a.u. for the matrix $\text{Li}_{1-x}\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ investigated experimentally in [21]. The spinel structure was assumed also for the solid mixture $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$. For example, in the case with $x=1$, for $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ by means of the Vegard law, the lattice constant $a=15.44$ a. u. was found for this solid solution concentration. The calculated internal parameter u for the perfect $\text{Li}_2\text{Mn}_4\text{O}_8$ crystal is 0.388, which also is in outstanding agreement with the experimental value of $u=0.390$ [20]. And

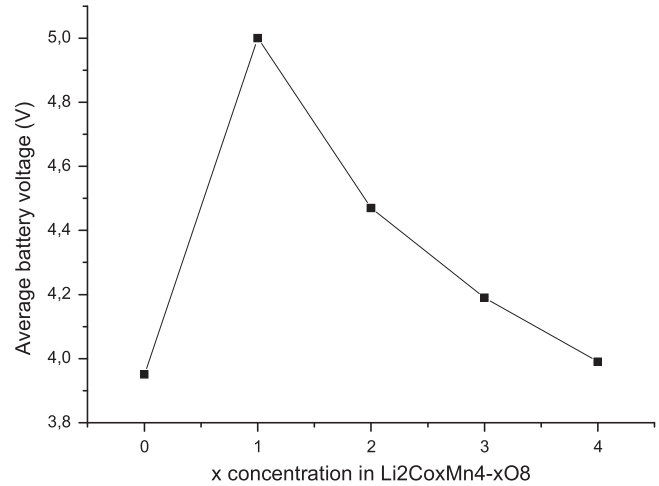
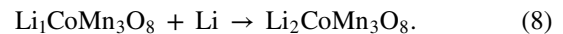


Figure 3. By means of the WIEN2k computer code, average battery voltages were calculated, using as a battery cathode material the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ for five different x concentrations ($x=0, 1, 2, 3, 4$).

finally, the internal parameter u for the hypothetical $\text{Li}_2\text{Co}_4\text{O}_8$ was predicted to be 0.389. As we can see from these results, there is practically no variation in the internal parameter u in the Mn-Co series.

The calculated average battery voltages for the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ are plotted in figure 3. They are calculated using equations (6)–(8). For example, the average battery voltage for the case with ($x=1$), which corresponds to $\text{Li}_2\text{CoMn}_3\text{O}_8$, was calculated as the total energy difference in the reaction



The total energies for the systems $\text{Li}_2\text{CoMn}_3\text{O}_8$ and $\text{Li}_1\text{CoMn}_3\text{O}_8$, as well as for the single Li atom, were calculated using the WIEN2k computer code. Since the supercell extension in the present WIEN2k calculations was ($1 \times 1 \times 1$), of course it was impossible to include any lattice relaxation around the Li vacancy in the $\text{Li}_1\text{CoMn}_3\text{O}_8$ system. In order to be sure that the calculated average battery voltage for the $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ cathode material is stable against interchange of the positions of Mn and Co atoms and also the position of the Li vacancy in this structure, all eight (4×2) possible geometrical configurations were calculated. The calculated average battery voltage using equation (8) for all eight configurations is in the range 4.90 V to 5.05 V, in other words, around 5 volts. The calculated average battery voltage for another x concentrations in the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ is considerably below 5 V (see figure 3). For example, the calculated average battery cathode voltage for the $\text{Li}_2\text{Co}_2\text{Mn}_2\text{O}_8$ is equal to 4.47 V. The calculated average battery cathode voltage for the $\text{Li}_2\text{Co}_3\text{MnO}_8$ is equal to 4.19 V. Finally, by means of the WIEN2k code, the calculated average battery cathode voltages for the end compounds with ($x=0$ and $x=4$) is equal to 3.95 and 3.99 volts, respectively (see figure 3).

Conclusions

Due to the rapid development of computers and cutting edge research methods, it is now possible to use a quantum mechanical electronic structure theory of solids to obtain, completely from first principles, the average voltage of a battery based on intercalation reaction energetics. Current commercially-available lithium ion batteries operate mostly in the 4 volt regime, and Ceder and his co-workers theoretically calculated [2–4] the average intercalation voltage for Li in LiCoO_2 compounds in the $\alpha\text{-NaFeO}_2$ structure to be 3.75 volts, very close to this commercial voltage. Based on the current calculation results for the solid solution $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ as the battery cathode material, it was shown that for the case with $x=1$, the $\text{Li}_2\text{CoMn}_3\text{O}_8$ battery cathode material can lead to a lithium ion battery operating at 5 volt regime. The calculated average battery voltages for another x concentrations ($x=0, 2, 3$ and 4) are equal to (3.95 V; 4.47 V; 4.19 V and 3.99 V) which is considerably below 5 volts.

Over recent years, indeed, such 5 volt batteries have also been designed experimentally by several groups around the globe. For example, Kawai *et al* [12, 13] reported the first single-cell lithium ion battery system to operate over 5 volts for a significant period of discharge, by incorporating a new battery cathode material, $\text{Li}_2\text{CoMn}_3\text{O}_8$. This result was independently confirmed by Yoon *et al* [14], who synthesized the $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($M=\text{Ni, Co, Cr}$) cathode materials by the solid state route. The authors found that these cathode materials showed a discharge plateau starting at around 5 volts [14, 16], and operate for a significant period of discharge at the 4.7 volt regime. The latest experimental results dealing with potential 5 volt battery cathode materials are published in [22–24]. The most recent experimental work performed recently by Hu *et al* [22–24] reports progress in high-voltage lithium ion batteries, and gives additional experimental support to 5 volt lithium ion batteries. The experimental results reported by Hu *et al* [22–24] are in general agreement with *ab initio* calculations performed in this paper. For example, Hu *et al* [22] experimentally prepared porous hollow LiCoMnO_4 microspheres combining porous structures in the surface and hollow structures inward, and used them as cathode materials for 5 volt lithium ion batteries, which exhibited good cyclic stability and rate capability.

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References

- [1] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 *Mater. Res. Bull.* **15** 783
- [2] Ceder G, Chiang Y M, Sadoway D R, Aydinol M K, Jang Y I and Huang B 1998 *Nature* **392** 694
- [3] Ceder G 1998 *Science* **280** 1099
- [4] Aydinol M K, Kohan A F, Ceder G, Cho K and Joannopoulos J 1997 *Phys. Rev. B* **56** 1354
- [5] Wolverton C and Zunger A 1998 *J. Electrochem. Soc.* **145** 2424
- [6] Deiss E, Wokaun A, Barras J L, Daul C and Dufek P 1997 *J. Electrochem. Soc.* **144** 3877
- [7] Benco L, Barras J L, Atanasov M, Daul C A and Deiss E 1998 *Solid State Ion.* **112** 255
- [8] Eglitis R I and Borstel G 2005 *Phys. Status Solidi a* **202** R13
- [9] Xia Y, Zhou Y and Yoshio M 1997 *J. Electrochem. Soc.* **144** 2593
- [10] Jang D H, Shin J Y and Oh S M 1996 *J. Electrochem. Soc.* **143** 2204
- [11] Gummow R J, Dckock A and Thackeray M M 1994 *Solid State Ion.* **69** 59
- [12] Kawai H, Nagata M, Tukamoto H and West A R 1998 *Electrochem. Solid State Lett.* **1** 212
- [13] Kawai H, Nagata M, Tukamoto H and West A R 1998 *J. Mater. Chem.* **8** 837
- [14] Yoon Y K, Park C W, Ahn H Y, Kim D H, Lee Y S and Kim J 2007 *J. Phys. Chem. Solids* **68** 780
- [15] Wei Y, Kim K B and Chen G 2006 *Electrochim. Acta* **51** 3365
- [16] Singhal R, Aries J J S, Katiyar R, Ishikawa Y, Vilkas M J, Das S R, Tomar M S and Katiyar R S 2009 *J. Renew. Sustain. Energy* **1** 023102
- [17] Ceder G, Kohan A F, Aydinol M K, Tepesch P D and Van der Ven A 1998 *J. Am. Ceram. Soc.* **81** 517
- [18] Ceder G 1993 *Comput. Mater. Sci.* **1** 144
- [19] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k—An Augmented PLane Wave + Local Orbitals Programm for Calculating Crystal Properties* ed K Schwarz (Austria: Technical University Wien)
- [20] Koyama K, Tanaka I, Adachi H, Uchimoto Y and Wakihara M 2003 *J. Electrochem. Soc.* **150** A63
- [21] Choi S and Manthiram A 2002 *J. Solid Chem.* **164** 332
- [22] Hu M, Tian Y, Wei J, Wang D and Zhou Z 2014 *J. Power Sources* **247** 794
- [23] Hu M, Tian Y, Su L, Wei J and Zhou Z 2013 *ACS Appl. Mater. Interfaces* **5** 12185
- [24] Hu M, Pang X and Zhou Z 2013 *J. Power Sources* **237** 229