

Towards a practical rechargeable 5 V Li ion battery

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Current lithium-ion batteries are the state-of-the-art power sources for consumer electronics operating mainly in the 4 V regime. One frequently discussed direction to improve the performance of such batteries is the development of a family of 5 V cathode materials. We report here a Full Potential

Linearized Augmented Plane Wave (FP-LAPW) calculation for $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ in the Fd3m spinel structure. Our calculated battery voltage for this material is around 5 V. This result is stable against interchange of positions of Mn and Co atoms as well as the choice of the position of the Li vacancy.

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1 Introduction The predictive power of first principles quantum electronic structure calculations due to increased speed of computers and recent developments of new and powerful computational methods allows for the rational design of new materials for technology applications on paper. One good example is the recent prediction of the average battery voltage for a series of a cathode materials from first principles calculations by Ceder [1, 2].

The lithium-ion battery, also referred to as rocking chair, shuttle cock, or intercalation battery [3, 4] is a promising advanced rechargeable battery. In 1989 the first commercial battery of this type was presented by Sony [5, 6]. Further battery improvements are anticipated concerning the environmental compatibility, energy density, specific energy, power density, specific power, cycling behaviour and cost.

Although lithium batteries have the highest energy density of all rechargeable batteries and are favoured in applications where low weight or small volume are desired – for example, laptop computers, cellular telephones and electric vehicles [4], the limitation of present commercial lithium batteries is the high cost of the LiCoO_2 cathode material. Searches for a replacement material that, like LiCoO_2 , intercalates lithium ions reversibly have covered most of the known lithium/transition-metal oxides, but the number of possible mixtures of these materials [7–9] is almost limitless.

Experiments in this area require an immense amount of time and manpower for synthesis, characterization and cycling. Since first principles quantum chemistry can now predict physical and chemical properties of molecules and solids, attempts should be made to use this tool for predicting favorable new electrode materials, thereby avoiding needless experimentation and focusing work solely on materials that promise success.

In what follows we concentrate on solid mixtures of LiMn_2O_4 and LiCo_2O_4 . Since both LiMn_2O_4 and LiCo_2O_4 have already been shown to exhibit a calculated average voltage near 4 V, which agrees quite well with experimental data [10], such mixtures constitute a promising class of materials. Recent experimental results show that for example $\text{Li}_2\text{FeMn}_3\text{O}_8$ [11] and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [12] are prospective 5 volt materials for advanced lithium ion batteries.

The hypothetical intercalation voltage in Li_xAlO_2 was calculated by Ceder et al. [2] and found to be 5.4 V. LiAlO_2 has empty Al *p* orbitals well above the filled oxygen *p* states with no *d* states in between (as have all the transition-metal oxides) and electron exchange therefore occurs completely with the oxygen bands [2]. Experimentally, this Li intercalation capacity will probably not be accessible as LiAlO_2 is electronically insulating.

For $\text{Li}(\text{Al}_{0.33}\text{Co}_{0.67})\text{O}_2$ and $\text{Li}(\text{Al}_{0.67}\text{Co}_{0.33})\text{O}_2$ in the $\alpha\text{-NaFeO}_2$ structure first-principles calculations by Ceder et al. published in *Nature* [2] predict an average Li intercalation potential of respectively 4.2 and 4.7 V.

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Cells with high operating voltage have been reported with cathodes based on spinel structure oxides, including 4.7 V for $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ [13, 14], 4.8 V for LiNiVO_4 [15] and $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ [16] and 4.9 V for $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ [17].

Kawai et al. [18] recently reported the first single-cell lithium battery system to operate over 5 V for a significant period of discharge, by the incorporation of a new cathode material, $\text{Li}_2\text{CoMn}_3\text{O}_8$ [19]. Discharge performance was limited to ca. 40 mAh g^{-1} at 5.0 V, but nevertheless this indicates the possibilities for developing practical 5 V batteries provided suitable cathodes can be prepared.

2 Results of computer simulations and discussion Ideal $\text{Li}_2\text{Mn}_4\text{O}_8$ has a cubic lattice, with symmetry group $\text{Fd}\bar{3}\text{m}$ (no. 227, spinel-type) containing 14 atoms per primitive cell. It is known to be antiferromagnetic, but so far no experimental information on the electronic or magnetic structure around Li or other defects in LiMn_2O_4 is available. The difference in calculated total energies between antiferromagnetic and ferromagnetic LiMn_2O_4 has been found to be as small as 0.02 eV [20]. Therefore one may safely assume that differences in the magnetic structures around Li defects will not significantly influence the relative stability. Thus, at a 0.2 V scale of precision, which seems to be a typical for present-day computational methods [21, 22], the prediction of intercalation voltages in such systems using *ab initio* methods on the basis of the local spin density approximation (LSDA) or the generalized gradient approximation (GGA) should be possible, independent of the detailed magnetic and/or correlation aspects in the bulk material.

We have performed our numerical calculations using the Full Potential Linearized Augmented Plane Wave (FPLAPW) computer code WIEN2k [23] for spin-polarized (ferromagnetic) mixtures of $\text{Li}_2\text{Mn}_4\text{O}_8$ and $\text{Li}_2\text{Co}_4\text{O}_8$, treating exchange and correlation effects within the Generalized Gradient Approximation (GGA). We performed spin polarized calculations. We used a Brillouin zone integration over 125 k points and muffin tin radius of 1.9 a.u. for Mn and Co and 1.7 a.u. for Li and O, respectively. From the calculated total energy we find the lattice constant a for ideal $\text{Li}_2\text{Mn}_4\text{O}_8$ to be 15.51 a.u., which is in very good agreement with the experimental data of 15.57 a.u. [24]. For the hypothetical ideal $\text{Li}_2\text{Co}_4\text{O}_8$ spinel a lattice constant of 15.22 a.u. is predicted, which compares well with experimental data of 15.10–15.12 a.u. for the system $\text{Li}_{1-x}\text{Co}_x\text{O}_{4-\delta}$ in Ref. [25]. Assuming the spinel structure also for the solid mixture $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ and using the Vegard rule, we find the lattice constant $a = 15.44$ a.u. for this mixture. The internal parameter u for the perfect $\text{Li}_2\text{Mn}_4\text{O}_8$ crystal was calculated to be 0.388, also in excellent agreement with the experimental value of $u = 0.390$ [24]. Our predicted internal parameter u for hypothetical $\text{Li}_2\text{Co}_4\text{O}_8$ is 0.389, i.e. according to this result there is essentially no variation of u in the Mn–Co series.

The average battery voltage for the $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ was calculated from the energy change in the reaction



In our calculations we have neglected any relaxation of the lattice around the Li vacancy in $\text{Li}_1\text{Co}_1\text{Mn}_3\text{O}_8$. Taking into account the results of other calculations for similar systems we expected that this assumption could result in an underestimation up to 0.2 V for the calculated potential [22]. But in order to ensure that the calculated average battery voltage is stable against interchange of the positions of Mn and Co atoms as well as the position of the Li vacancy in the $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ structure, we have tested all eight (4×2) possible geometrical configurations. The average voltage, as calculated from Eq. (1), has been found for all configurations in the range of 4.90 V to 5.05 V, i. e. close to 5 V.

Like in the case of other complex oxidic materials, exact stoichiometry is difficult to obtain in the $\text{Li}_2\text{Co}_x\text{Mn}_{4-x}\text{O}_8$ series. Nonstoichiometry means defect formation, which in such systems according to several experimental and theoretical studies involves mainly defects of oxygen-vacancy type and of metal (Li, Mn, Co) interstitial type. According to very recent calculations of oxygen-deficient LiMn_2O_4 [24] the simple oxygen vacancy shows the highest stability among the oxygen-vacancy-type defects, but metal-excess defects, in particular Li excess, are even more stable. Clearly such possibilities of defect formation should be taken into account in future calculations of the average voltage. In particular the Li excess is interesting, since it is known that Li excess improves the capacity fading during the charge-discharge cycles in such batteries. However, at present it is not clear, if such refinements will result in corrections beyond 0.2 V.

3 Conclusions Due to increased speed of computers and recent development of new and very exact computational methods, it is possible to design new materials and devices for technology applications on paper. Currently available lithium-ion batteries are operating mainly in the 4V regime. Based on our calculations, we show that a $\text{Li}_2\text{Co}_1\text{Mn}_3\text{O}_8$ cathode material can lead to a lithium-ion battery operating at 5 V regime.

Indeed, recently by Kawai et al. [18, 19] was reported the first single-cell lithium battery system to operate over 5 V for a significant period of discharge, by incorporation of a new cathode material, $\text{Li}_2\text{CoMn}_3\text{O}_8$. Discharge performance was limited to ca. 40 mAh g^{-1} at 5 V [18], but nevertheless this indicates the possibilities for developing practical 5 V batteries.

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References

- [1] G. Ceder, *Science* **280**, 1099 (1998).
- [2] G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang, and B. Huan, *Nature* **392**, 694 (1998).
- [3] K. Brandt, *Solid State Ion.* **69**, 173 (1994).

- [4] G. Pistoia (Ed.), *Lithium Batteries*, Industrial Chemistry Library, Vol. 5 (Elsevier, Amsterdam 1994).
- [5] T. Nagaura, M. Nagamine, I. Tanabe, and M. Miyamoto, *Progr. Batt. Sol. Cells* **8**, 84 (1989).
- [6] K. Ozawa, *Solid State Ion.* **69**, 212 (1994).
- [7] C. Delmas and I. Saadoune, *Solid State Ion.* **53–56**, 370 (1992).
- [8] J. N. Reimers, E. Rosen, C. D. Jones, and J. R. Dahn, *Solid State Ion.* **61**, 335 (1993).
- [9] T. Ohzuku, T. Ueda, A. Nagayama, M. Iwakoshi, and H. Komori, *Electrochem. Acta* **38**, 1159 (1993).
- [10] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [11] H. Kawai, M. Nagata, M. Tabuchi, H. Tukamoto, and A. R. West, *Chem. Mater.* **10**, 3266 (1998).
- [12] T. Ohzuku, S. Takeda, and M. Iwanaga, *J. Power Sources* **81**, 90 (1999).
- [13] Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, and J. R. Dahn, *J. Electrochem. Soc.* **144**, 205 (1997).
- [14] K. Amine, H. Tukamoto, H. Yasuda, and Y. Fujita, *J. Power Sources* **68**, 604 (1997).
- [15] G. T.-K. Fey, W. Li, and J. R. Dahn, *J. Electrochem. Soc.* **41**, 2279 (1994).
- [16] C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard, and M. Tournoux, *Solid State Ion.* **81**, 167 (1995).
- [17] Y. Ein-Eli, W. F. Howard, Jr., S. H. Lu, S. Mukerjee, J. McBreen, J. T. Vaughey, and M. M. Thackeray, *J. Electrochem. Soc.* **145**, 1283 (1998).
- [18] H. Kawai, M. Nagata, H. Tukamoto, and A. R. West, *Electrochem. Solid-State Lett.* **1**, 212 (1998).
- [19] H. Kawai, M. Nagata, H. Tukamoto, and A. R. West, *J. Mater. Chem.* **8**, 837 (1998).
- [20] S. K. Mishra and G. Ceder, *Phys. Rev. B* **59**, 6120 (1999).
- [21] G. Ceder, M. Aydinol, and A. Kohan, *Comput. Mater. Sci.* **8**, 161 (1996).
- [22] M. Aydinol, A. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, *Phys. Rev. B* **56**, 1354 (1997).
- [23] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k – An Augmented Plane Wave + Local Orbitals Programm for Calculating Crystal Properties* (Karlheinz Schwarz, Technical University Wien, Austria, 2001).
- [24] K. Koyama, I. Tanaka, H. Adachi, Y. Uchimoto, and M. Wakihara, *J. Electrochem. Soc.* **150**, A63 (2003).
- [25] S. Choi and A. Manthiram, *J. Solid Chem.* **164**, 332 (2002).