

Ab initio calculation of the intercalation voltage of lithium-transition-metal oxide electrodes for rechargeable batteries

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Abstract

A first-principle's method to predict the intercalation voltage for lithium in metal oxides is presented. Although the intercalation voltage for lithium is often related to aspects of the electronic structure, this voltage can only be accurately calculated from the lithium chemical potential in the anode and cathode. Using the pseudopotential technique the average intercalation voltage of LiMO_2 cathodes is computed for $M = \text{Ti, V, Co, Ni}$ and Cu . Although no experimental data are used as input, agreement with experiment is good, indicating the potential to use this method to predict the properties of new compounds. © 1997 Elsevier Science S.A.

Keywords Lithium batteries, Battery voltage; Pseudopotential, Cathodes, Lithium-metal oxides, First-principle's calculation

1. Introduction

Rechargeable lithium batteries are attractive for their potential as lightweight, compact energy storage devices in applications ranging from portable electronics to electrical vehicles [1]. Their economic success will ultimately depend on the inexpensive and safe design of the three major components (anode, electrolyte and cathode). The efficient development of each of these components depends critically on our understanding of the relation between chemistry, structure, and properties. The focus of this paper is on the lithium-metal oxide compounds which constitute the active component of the cathode. We will show that first-principle's calculations can be used to predict the average intercalation voltage of different compounds. By investigating properties of novel compositions and structures before time is invested in synthesis and characterization, first-principle's modeling is an efficient way to search for optimized intercalation compounds. Computational 'experiments' also offer a unique level of control over the structure and chemistry of the system under study. Whereas in experimental investigations these two variables are coupled, their effect on voltage can be studied separately with ab initio computations.

The thermodynamic voltage in a lithium battery is determined by the chemical potential difference for lithium ions in the anode and cathode. The high chemical potential on the

anode side is usually established by pure lithium metal, a lithium-metal alloy, or by a solution of lithium in carbon. On the cathode side, many different compounds can be used for the low chemical potential reservoir. Whereas originally metal sulfides (e.g. TiS_2 , MoS_2) [2] were investigated as cathode materials, interest has shifted towards the lithium-transition metal oxides (Li_xMO_2). These compounds are more oxidizing towards lithium, resulting in a higher intercalation voltage and energy density. Compounds such as Li_xCoO_2 [3], Li_xNiO_2 [4] and $\text{Li}_x\text{Mn}_2\text{O}_4$ [5] intercalate lithium around 4 V. In addition, lithium can be reversibly cycled in and out without major structural changes, making these materials highly suitable for secondary battery applications. Several mixtures of transition metals have also been investigated [6–9].

Most of the LiMO_2 compounds can be considered as ordered rock-salt structures [10,11] but the compounds differ widely by the type of cation ordering in the octahedral sites. Because of these structural variations, it is difficult to separate the effect of structure from that of chemistry (choice of M) in experimentally determined properties. With first-principle's calculations these variations can be studied independently. For example, in this paper we will study how the choice of M influences the intercalation voltage, while keeping the structure type the same. This will allow us to isolate the effect of chemistry on voltage. The structure used in the calculations is the α - NaFeO_2 structure (Fig. 1). This is a layered structure found in LiCoO_2 , LiNiO_2 and LiVO_2 . The

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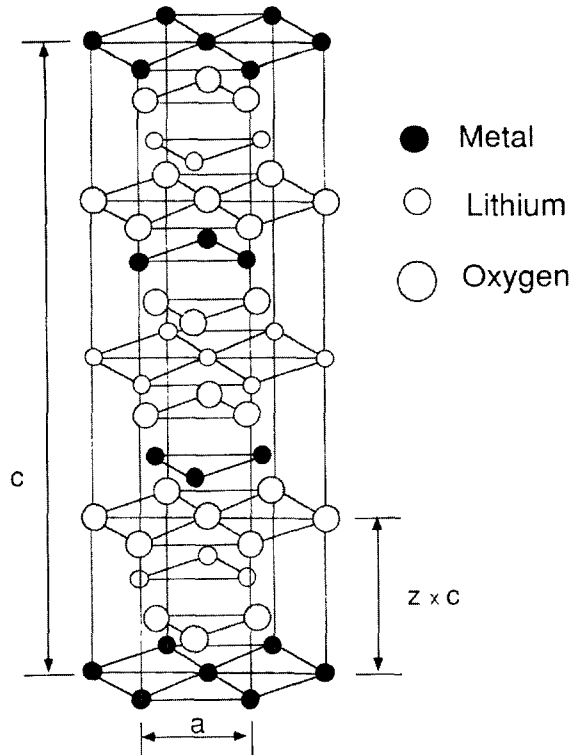


Fig. 1. Unit cell of the LiMO_2 structure in hexagonal setting.

MO_2 units form strongly bonded sandwiches between which the lithium ions intercalate. It is believed that this layering of the structure allows for the easy removal or incorporation of lithium ions.

2. Methodology

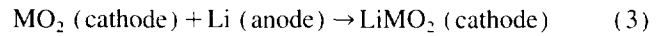
Attempts have been made to derive the intercalation voltage of ions from the electronic structure of the host material [12,13], and in particular from the location of the Fermi level. Such approximations are inherently flawed as they only deal with the contribution of the electron to the electrochemical work. As pointed out by McKinnon [14], any separation of the intercalation energy into an electronic and ionic part is arbitrary due to the strong interaction between the intercalated Li^+ ion and the extra electron. More rigorously, the equilibrium intercalation voltage depends on the chemical potential difference for lithium in the anode and cathode material [15]

$$V(x) = \frac{\mu_{\text{cathode}}^{\text{Li}}(x) - \mu_{\text{anode}}^0}{zF} \quad (1)$$

In this work we will assume an anode of metallic lithium, but the results can be easily modified for other anodes. The lithium chemical potential is the partial derivative of the free energy of the cathode material with lithium composition, x . In this paper we will not compute the voltage as a function of x , but rather determine the average voltage for a full cycle between the compositions LiMO_2 and MO_2 . This voltage can be determined from the Nernst equation

$$V(x) = \frac{-\Delta G_r}{zF} \quad (2)$$

where z is the charge on the lithium ion in the electrolyte ($z = 1$) and ΔG_r is the Gibbs free energy for the reaction



Volume effects and entropic effects will be neglected so that $\Delta G_r (\equiv \Delta E_r + P\Delta V_r - T\Delta S_r)$ can be approximated by the change in internal energy (ΔE_r) at 0 K. The term $P\Delta V_r$ is of the order 10^{-5} eV whereas ΔE_r is of the order of 3 to 4 eV per molecule. The term $T\Delta S_r$ is of the order of the thermal energy which is also much smaller than ΔE_r .

Eq. (3) indicates that the total energy of three compounds is required to predict the average intercalation voltage. The accurate calculation of total energies of materials represents one of the prime challenges of condensed matter physics. The method used in this work is the pseudopotential technique, with exchange and correlation in the 'local density approximation' (LDA). The LDA has a considerable track record [16–18] in predicting the properties of metals, semiconductors and oxides [19]. A recent study on the CaO-MgO system also showed that formation energies are accurate on the scale of thermal energy [20]. In the pseudopotential method implementation of the LDA only the valence electrons are explicitly calculated. The core electrons are not included in the calculation and the effect of the frozen core (nucleus + core electrons) is represented by the pseudopotential. The wave functions of the valence electrons are expanded in plane waves. This prevents any bias towards the shape of the electron density, a problem that often occurs with other techniques. We found that methods in which a spherical shape is imposed on the single electron potential, although much less computer intensive, do not adequately predict the total energy of oxides. We use norm-conserving optimized pseudopotentials of the Kleinman–Bylander type [21] with the exchange correlation energy as parameterized by Perdew and Zunger [22]. For more details on the method see the work by Payne [17]. The energy cutoff for the plane wave expansion was 900 eV and reciprocal space sampling was done with 27 k -points in the irreducible Brillouin zone using a broadening of 0.01 eV for the systems that have partially filled bands. Details of the pseudopotential calculations will be offered in a forthcoming paper. Because of its low nuclear charge the (1s) core states of lithium overlap with (2s) and change in energy when going from the atomic state to the metallic state. These core corrections add 0.22 eV/atom to the cohesive energy of lithium metal [23]. Rather than perform a full electron calculation for lithium we simply added 0.22 eV/atom to the energy of lithium metal obtained with the pseudopotential method. This correction shifts all the voltages up by the same amount. The core corrections are not expected to be important for the Li^+ ion (as there is no valence electron to interact with the core).

One of the advantages of the pseudopotential method is that it allows one to determine the total energy of a material

and therefore also the intercalation voltage. This is not the case with methods that only determine the band part of the energy.

To determine the average intercalation voltage for a given choice of M, the total energy of three structures is required: metallic lithium in body centered cubic and the oxide structures before and after intercalation. The energies of Li_xMO_2 with $x = 1$ and $x = 0$ are calculated in the $\alpha\text{-NaFeO}_2$ structure (Fig. 1) with and without lithium ions. The symmetry of this structure is $R\bar{3}m$. Three degrees of freedom exist: the a - and c -lattice parameters and the internal coordinate z , see Fig. 1. To obtain the minimum energy of the compound the structure has to be relaxed to the values of a , c and z that give the lowest possible energy. Typically, one total energy calculation requires approximately 1 h on a Cray C90 supercomputer. Approximately 25–30 total energy calculations are needed to find the equilibrium values of a , c and z .

3. Results

Table 1 shows the intercalation energy in the $\alpha\text{-NaFeO}_2$ structure for five different metals. Although only three of these compounds (LiNiO_2 , LiCoO_2 and LiVO_2) are known to exist in the $\alpha\text{-NaFeO}_2$ structure, the purpose of the calculations is to investigate the effect of chemistry on the cathode voltage, other parameters being equal. This is why we opt for one common structure in the calculations. The real LiTiO_2 forms a more complex structure and LiCuO_2 is not stable [11]. The average voltage increases from titanium to cobalt, then drops at nickel and increases again in going to copper.

The computed lattice parameters are given in Table 2. Where available, the experimental values are given in parenthesis. It can be seen that the lattice parameters and the cell

Table 1
Average intercalation voltage for different LiMO_2 compounds (calculated in the $\alpha\text{-NaFeO}_2$ structure)

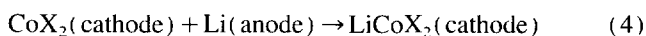
M	Ti	V	Co	Ni	Cu
Average voltage (V)	2.36	3.03	3.97	3.14	3.88

Table 2
Crystallographic parameters for different LiMO_2 materials in the $\alpha\text{-NaFeO}_2$ structure. Experimental data are given in parenthesis (from Refs. [4,8,34])

	a (Å)	c (Å)	z	V (Å ³)
TiO_2	3.01	12.8	0.255	34.5
LiTiO_2	2.98	14.1	0.250	36.1
VO_2	2.88	12.4	0.248	29.7
LiVO_2	2.88 (2.84)	14.2 (14.7)	0.251	34.0 (32.23)
CoO_2	2.88	12.3	0.259	29.4
LiCoO_2	2.93 (2.82)	13.2 (14.04)	0.260 (0.264)	32.7 (34.9)
NiO_2	2.87 (2.814)	11.7 (13.47)	0.255	27.8 (30.79)
LiNiO_2	2.99 (2.88)	12.85 (14.19)	0.258 (0.259)	33.2 (34.0)
CuO_2	2.98	11.2	0.253	28.7
LiCuO_2	3.05	12.7	0.256	34.1

volumes are predicted reasonably well by the pseudopotential method.

We also investigated the effect of substituting the anion. In this series of calculations we computed the formation energy of the reaction



where X is O, S or Se. The results are given in Table 3. Clearly, the heavier anions reduce the intercalation voltage.

First-principle's methods make it possible to study the electronic changes that occur upon intercalation in great detail. From the plane wave expansion, the electronic wave functions can be constructed and the charge density plotted. To investigate the charge transfer associated with lithium intercalation we plot in Fig. 2 the difference between the charge density in LiCoO_2 and CoO_2 in the (110) plane defined by a lithium, oxygen and cobalt ion. For the purpose of this calculation we computed the charge density for both LiCoO_2 and CoO_2 in exactly the same geometry. This makes it possible to subtract the electron densities point by point. Fig. 2 can therefore be thought of as the change in electron density upon inserting a lithium atom in an otherwise frozen structure. Clearly, a substantial fraction of the electron from lithium is transferred into a charge cloud around oxygen. By integrating the charge-transfer density around oxygen and cobalt we find a transfer of about 0.25 electrons to each oxygen and 0.28 electrons to cobalt. The remaining 0.22 electrons are in the interstitial space. We find similar electron-

Table 3
Average voltage for different LiCoX_2 compounds

X	O	S	Se
Average voltage (V)	3.97	2.36	1.68

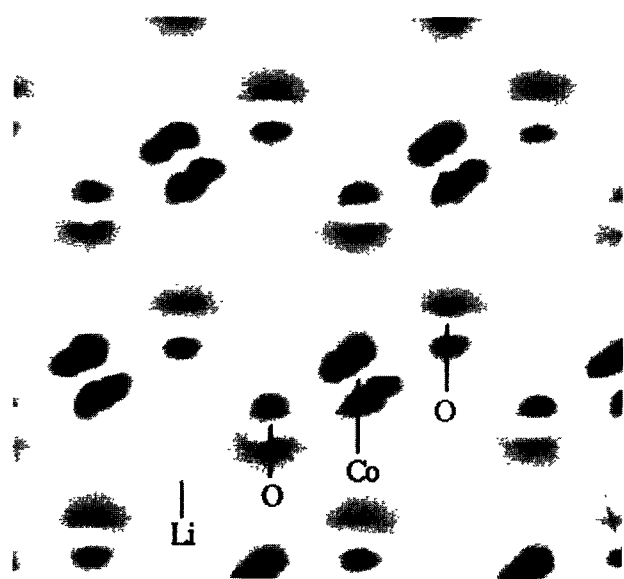


Fig. 2. Difference in charge density between the lithiated material (LiMO_2) and the unlithiated material (MO_2). The plane shown is parallel to the c -axis and contains lithium, oxygen and cobalt ions.

transfer behavior in the other compounds, with the transfer to oxygen increasing monotonically from $M = \text{Ti}$ to $M = \text{Cu}$. The large electron transfer to oxygen instead of to the transition metal as lithium is intercalated is not that unusual. Using *K*-edge X-ray absorption spectroscopy and X-ray photoemission spectroscopy on $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (with $0 < x < 0.5$) several authors have argued that lithium substitution introduces a hole on the oxygen rather than on nickel [24–27]. Removing lithium from LiNiO_2 can be seen as the further removal of electrons from the oxygen ions. Similar results have been obtained by Umrigar et al. [28] in LiTiS_2 .

4. Discussion

By computing the energy of a few ordered compounds the average intercalation voltage in a system can be predicted. Because of the *ab initio* nature of these calculations, no experimental data are required to predict the voltage in a new system. Although the objective of this paper is to present a series of computational experiments to establish the correlation between composition and voltage without interference from structural changes, a comparison of some of the numbers in Table 1 with experimental data is in order. Discrepancies between calculation and experiment can arise both from approximations in the pseudopotential method or from limitations in the assumptions we made regarding structures and intercalation limits. Only LiVO_2 and LiCoO_2 form the α - NaFeO_2 structure. For the other materials any comparison between calculated and measured voltages is obviously precluded. Although it is often stated that LiNiO_2 also forms the α - NaFeO_2 structure it was recently shown that a Jahn–Teller distortion locally modifies the structure by deforming the oxygen octahedra around the Ni^{3+} ion [29,30]. Since the distortion is not cooperative, the symmetry of LiNiO_2 is observed to be the same as that of α - NaFeO_2 in some experiments. By lowering the energy of LiNiO_2 the Jahn–Teller mechanism increases the intercalation voltage from what would be obtained with LiNiO_2 in the perfect α - NaFeO_2 structure (which is what is computed in Table 1). For $M = \text{Co}$, the predicted voltage compares extremely well to experimental results (typically around 4 V [8]) indicating the accuracy of our approach. The results also predict that if LiCuO_2 were stable it would have an intercalation voltage comparable to that of the cobalt system.

The average voltage listed in Table 1 is based on intercalation from MO_2 to LiMO_2 . Practically, the MO_2 composition is never reached experimentally due to decomposition problems of the electrolyte and the cathode material. This leads to a systematic omission of the higher voltage part of the intercalation cycle. Calculated average voltages may therefore be slightly higher than the experimentally determined ones. Our approach can, in principle, be applied to compute the average intercalation voltage between any two intercalation limits by computing the energy of structures with different lithium composition. This is more difficult since the

structures where X_{Li} is not equal to 1 or 0 are either non-periodic on the atomistic scale (due to the disorder on the lithium sites) or have a large periodicity (if lithium orders into superstructure arrangements). Although the general formalism to incorporate such disorder exists [31,32], such calculations are currently infeasible with the pseudopotential method due to the large amount of computing time required for a single calculation. However, progress may be made with simpler methods [33].

The substantial charge transfer from lithium to oxygen may at first be surprising. It can be understood from the close proximity of the oxygen *p* and metal *d* levels for the late transition metals.

Table 1 shows a remarkably small variation between the average intercalation voltage for different transition metals. Only $M = \text{Ti}$ is outside the 3 to 4 V range. This may indicate that differences in crystal structure are at least partly responsible for the experimentally observed variations. Future work will therefore focus on the effect of structure on the average intercalation voltage. These results open up the possibility of many different metal chemistries for intercalation cathodes, if they can be synthesized in the correct structure.

5. Conclusions

First-principle's techniques can be used to estimate the average voltage of metal oxide cathodes for lithium batteries. Computer 'experiments' of the type presented here, whereby structural variations are eliminated, allow us to gain insight into the factors that relate chemistry and intercalation voltage. Because of the *ab initio* nature of these calculations, no experimental input is required to predict the intercalation voltage, so that new materials can be assessed without spending time synthesizing them.

At this point, an accurate prediction of the intercalation voltage requires a substantial amount of computing time. However, with the accuracy of simpler, interpolating schemes being established [33], it should be possible to predict phase transitions and electrochemical properties during charge and discharge cycles.

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