ANL/CMT/CP - 97216

FIRST-PRINCIPLES CALCULATION OF ATOMIC STRUCTURE AND ELECTROCHEMICAL POTENTIAL OF $Li_{1+x}V_3O_8$

R. Benedek and M. M. Thackeray
Electrochemical Technology Program, Chemical Technology Division
Argonne National Laboratory
Argonne, IL U.S.A.

and

L. H. Yang
Lawrence Livermore National Laboratory
Livermore, CA U.S.A.

RECEIVED
SEP 28 1999
OSTI

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

July 1998

To be presented at the 9th International Meeting on Lithium Batteries, Edinburgh, Scotland, United Kingdom, July 12-17, 1998

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FIRST-PRINCIPLES CALCULATION OF ATOMIC STRUCTURE AND ELECTROCHEMICAL POTENTIAL OF $Li_{1+x}V_3O_8$

R. Benedek* and M. M. Thackeray
Electrochemical Technology Program, Chemical Technology Division
Argonne National Laboratory
Argonne, IL U.S.A.
and
L. H. Yang
Lawrence Livermore National Laboratory
Livermore, CA U.S.A.

Keywords: vanadium oxide, structure, first-principles, calculation

Abstract

Interest in the γ-bronze, $Li_{1+x}V_3O_8$, as a possible electrode material in rechargeable Li batteries has stimulated several experimental studies on this system. Detailed interpretation of the electrochemical and physical-property measurements is complicated by uncertainties regarding the structural arrangement of Li atoms as a function of x and by a phase transition between two monoclinic structures (γ_a , γ_b) during intercalation. To elucidate the atomic structures and the phase transition, first-principles calculations are performed with the local-density-functional-theory (LDFT) planewave pseudopotential method for both γ_a and γ_b as a function of lithiation. Calculations for the compositions $1 + x = 1.5$ and $1 + x=4$ confirm that the Li configuration determined in the existing x-ray diffraction structure refinements (at $1 + x =1.2$ and $1 + x =4$ respectively), coincide with the predicted low-energy configurations. Structure predictions were made at intermediate compositions, for which no experimental structure measurement is available. The order in which the tetrahedrally coordinated Li sites are filled at equilibrium as a function of x in γ_a was predicted. Calculated electrochemical potentials as a function of composition agree well with experimental data.

* Corresponding author, e-mail: benedek @cmt.anl.gov; Tele: (630) 252-5063; FAX: (630) 252-7777

Introduction

The structural stability of the cathode under Li insertion/extraction is critical to the performance of Li batteries, and understanding the evolution of atomic structure during lithiation is a first step toward the design of improved materials. Experimental atomic structure characterization, for example by x-ray diffraction (XRD), is limited by the availability of homogeneous specimens, and measurements have primarily been restricted to special stoichiometries at which stable, ordered compounds occur. First-principles theory can complement experimental efforts in this regard and help to elucidate structural details of candidate battery materials. In particular, local-density functional theory [1] provides a robust framework for the parameter-free calculation of structural properties of materials. Some recent work along these lines has focused on lithiated transition metal dioxides [2,3]. This paper presents first-principles calculations for the layered trivanadate, the so-called γ-bronze $Li_{1+x}V_3O_8$[4], based on the planewave pseudopotential method [5]. The γ-bronze has a larger unit cell (25-30 atoms), and therefore requires greater computational effort than the dioxides. It has been under consideration as a possible cathode material [6-12], but its performance is degraded by a structural phase transition that occurs in the vicinity of $1 + x = 3$. Both the low- and high-Li phases (which we refer to as γ_a and γ_b , respectively) are monoclinic, but the former contains tetrahedrally as well as octahedrally coordinated Li. Differences between the lattice constants [4] of the two phases suggest that the transition is first order.

Internal energy vs. lithiation

To elucidate the $\gamma_a - \gamma_b$ phase transition, internal energy is calculated for both phases as a function of x. The planewave pseudopotential method [13] is well-suited to this task because it can more readily accommodate large unit cells than all-electron methods such as the full-potential linearized augmented planewave (FLAPW) method. The local-density-functional-theory framework reliably predicts total-energy related properties for many oxides, even though the method does not predict an insulating gap in the electronic density of states for the trivanadate system, which is known to be insulating [11]. The pseudopotential calculations employ a planewave cutoff energy of 70 ry, 16 special k-points Brillouin zone sampling, and Gaussian broadening.

The unit cell of $Li_{1+x}V_3O_8$ contains two formula units, with atoms located on two (010) layers stacked along the monoclinic *b*-axis; the coordinates on adjacent layers are related to each other by inversion symmetry. The lattice cell vectors in most of the calculations for γ_a (γ_b) are fixed at the experimental values for $1 + x = 1.2$ (4); however, for each composition the internal coordinates are relaxed using Hellmann-Feynman forces. Both the cell vectors and the internal coordinates were relaxed for the composition $Li_4V_3O_8$ (γ_b) and the resultant cell vectors were within 2% of experimental values.

A central result of this work is the energy per inserted Li as a function of composition of the two phases, which is plotted in Fig. 1. The reference composition was taken to be $x = 1$; the minimum Li content observed experimentally in this compound is 1.1- 1.2. The atomic structures employed in the calculations are described in the following section. We observe in Fig. 1 that the compositions predicted to be most stable are $x = 0+$ for γ_a and $x = 3$ for γ_b . Experimentally, these compositions (or very close to them) are the ones for which single crystal specimens are most readily synthesized and x-ray diffraction measurements are available [4]. Mean deviations of calculated relaxed atomic positions from measured values for these compositions (Fig.2) are only about 0.15 Å. A similar level of agreement between theory and experiment is found for $Li_4V_3O_8$. The agreement between theory and experiment for the standard compounds gives us confidence in LDFT predictions for intermediate compositions.

The crossover between the γ_a and γ_b phases occurs at $1 + x = 3$. Since the transition is first order, transformation between the phases is determined partly by kinetics. From electrochemical potential measurements at a small current [14], the transition between the two phases is thought to occur approximately between $1 + x = 3$ and $1 + x = 4$.

Li site preference

In order to calculate the free energy for each composition represented in Fig. 1, the configuration of Li atoms must be determined. Experiments[4] indicate that the compositions $1 + x = 1.2$ (γ_a) and $1 + x = 3$ (γ_b) are well ordered. Although some disorder of the Li is likely to exist at other compositions, it appears reasonable to represent each composition by the lowest-energy ordered structure, although such a treatment neglects entropic free-energy contributions

and the kinetic barriers that may hinder the achievement of the lowest energy ordered structure in practice.

In the γ_a phase the octahedral sites designated Li(1) are occupied in the framework structure $Li_1V_3O_8$. To test the preference for Li(1) in the framework structure, calculations at this composition were also performed with the tetrahedral site $S_t(3)$ occupied instead and the energy was found to be higher by almost 1 eV per formula unit.

Additional Li atoms ($x > 0$) in the γ_a phase are accommodated in tetrahedral sites. The most prominent tetrahedral sites in this structure are illustrated in Fig.3. One of the sites labeled Li(2) is the first to be occupied, at $1 + x = 1.5$, but the next site to be occupied is not the other Li(2), but one of the $S_t(3)$ sites. This is followed (at $1 + x = 2.5$) by the other $S_t(3)$ site and then (at $1 + x = 3.0$) the filling of Li(2) is completed. Above $1 + x = 3.0$, $S_t(4)$ begins to be occupied.

In qualitative terms, the Li-filling sequence for the γ_a phase can be interpreted as follows. The structure of lithiated trivanadates is determined in general by a competition between two Li and V cations for oxygen bonds. Apart from this competition, octahedral sites with six bonds for Li would be favored over tetrahedral sites with four bonds. In the "unintercalated" framework structure, with composition $Li_1V_3O_8$, the cation distribution is sparse enough to enable Li to occupy octahedral sites, while allowing both LiO and VO bondlengths to be close to optimal. The first intercalants into this structure, however, prefer tetrahedral Li(2) sites, which enable four strong Li-O bonds to exist without significantly distorting the V-O bonds. Tetrahedral $S_t(3)$ sites are then occupied before the filling of the Li(2) is complete, reflecting a trade-off between Li-Li repulsion and Li-O bonding (more details on this will be presented elsewhere). As more tetrahedral sites become occupied, the γ_a phase becomes less favorable than the γ_b phase, because the V-O bonds are no longer significantly less distorted than they are in γ_b, in which the Li forms six Li-O bonds.

In the γ_b phase there are five inequivalent octahedral sites for Li, as illustrated in Fig. 4. At the most stable composition, $Li_4V_3O_8$, only one of them is vacant. The most symmetric location of this vacancy is the favored site: at $S_o(2)$, with Li dimers on either side. This configuration apparently minimizes interference between Li-O and V-O bonding. Structures for γ_b with $1+x < 4$ were obtained by depopulating sites in the order suggested by the vacancy

energies calculated for $Li_4V_3O_8$. The composition $Li_5V_3O_8$ is obtained by filling all five sites in Fig. 4 with Li. A calculation was also done for $Li_{5.5}V_3O_8$, with an additional Li placed interstitially between layers.

Electrochemical Potential

The differences between calculated total energies at intervals of $\Delta x = 0.5$ enable estimates of the Li chemical potential in the two phases of $Li_{1+x}V_3O_8$, and hence the cell electrochemical potential, which we take relative to a Li metal anode. The cell voltage is thus

$$V(x) = \mu(\text{Li,cathode}) - \mu(\text{Li,anode}),$$

where the cathode chemical potential

$$\mu(\text{Li,cathode}) \approx (E(1 + x + \Delta x/2) - E(1 + x - \Delta x/2))/\Delta x.$$

The numerical results are plotted in Fig. 5 along with experimental measurements [14]. As mentioned above, the regions below $1 + x \approx 3$ and above $1 + x \approx 4$ and are thought to be single phase, whereas the region from 3-4 is a mixture. The predicted $V(x)$ for the low-Li (γ_a) phase appears slightly low and that for the high-Li (γ_b) phase appears too high, but overall the magnitudes and trends are in reasonable accord with experimental results.

Discussion and Conclusions

We have applied local-density-functional theory to calculate atomic structures and total energies for the low- and high-Li phases of $Li_{1+x}V_3O_8$. The energy per inserted Li, a convenient measure of compound stability, was lowest for γ_a at $1 + x = 1.5$ and for γ_b at $1 + x = 4.0$. These results coincide closely with the compositions of each phase most readily synthesized experimentally. The γ_a phase at $1+x=1.5$ is particularly stable because the minimum Li-Li separation is relatively large, of order 3.8 Å; the structures of γ_a phase compounds in the range $1+x = 2$ to 3 have minimum Li-Li separation of about 2.5 Å. The energy plotted in Fig. 1 corresponding to $1+x=1.5$ lies below the extrapolation of a linear fit of the points at higher lithiation. The most stable composition of γ_b occurs at $1+x=4$. We suggest that a special stability is associated with the V^{4+} valence state with a single *d*-electron analogous to the stabilization resulting from a Jahn-Teller effect distortion. This interpretation, however, cannot directly be

demonstrated because no undistorted reference structure exists for this compound. The calculated equilibrium atomic coordinates for γ_a at $1 + x = 1.5$ and for γ_b at $1 + x = 4.0$ closely agree with x-ray diffraction results. This agreement gives us some confidence in the predictions made for other compositions. Experimental tests would be of interest.

Acknowledgments

We gratefully acknowledge support from the U.S. Department of Energy Advanced Battery Research Program, Chemical Sciences Division, Office of Basic Energy Sciences. L.H.Y. was supported at Lawrence Livermore National Laboratory by the U.S. Department of Energy under contract no. W-7405-ENG-48. Most of the computational work was performed at the National Energy Research Supercomputer Center, and at the Argonne National Laboratory IBM SP facility.

References

[1] R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* 61 (1989) 689.

[2] M. K. Aydinol, A. F. Kohan, G. Ceder, Y. Cho, and J. Joannopoulos, *Phys. Rev.* B56 (1997) 1354.

[3] C. Wolverton and A. Zunger, *Phys. Rev.* B 57 (1998) 2242.

[4] L. A. de Picciotto, K. T. Adendorff, D. C. Liles and M. M. Thackeray, *Solid State Ionics* 62 (1993) 297.

[5] Earlier reports on this work were given in R. Benedek, M. M. Thackeray, and L. H. Yang, *Phys. Rev.* B56 (1997) 10707, and R. Benedek, M. M. Thackeray, and L. H. Yang, in Mater. Res. Soc. Proceedings vol. 496 (1998) in press.

[6] K. West, B. Zachau-Christiansen, S. Skaarup, Y. Saidi, J. Barker, I. I. Olsen, R. Pynenburg, and R. Koksbang, *J. Electrochem. Soc.* 143 (1996) 820.

[7] J. Kawakita, H. Katagiri, T. Miura, T. Kishi, *J. Power Sources* 68 (1997) 680.

[8] S. Panero, M. Pasquali, and G. Pistoia, *J. Electrochem. Soc.* 130 (1983) 1225.

[9] G. Wang, J. Roos, D. Brinkmann, M. Pasquali and G. Pistoia, *J. Phys. Chem. Solids* 54 (1993) 851.

[10] R. Tossici, R. Marassi, M. Berrettoni, S. Stizza, and G. Pistoia, *Solid State Ionics* 57 (1992) 227.

[11] G. Pistoia, M. Pasquali, M. Tocci, V. Manev, and R. V. Moshtev, *J. Power Sources* 15 (1985) 13.

[12] X. Zhang and R. Frech, *Electrochimica Acta* 43 (1998) 861.

[13] M. C. Payne, M. P. Teter, D. C. Allan, T. P. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* 64 (1992) 1045.

[14] V. Battaglia, A. Jansen, and A. Kahaian, unpublished data (1997).

Figure captions

Fig. 1. Calculated total energy per inserted Li [$\Delta E = (E(1+x) - E(1))/x$] vs. lithiation for γ_a (low-Li) and γ_b (high-Li) phases.

Fig. 2. Calculated and measured atomic positions for γ_a at $x = 1.5$.

Fig. 3. Candidate tetrahedral sites in the low-Li γ_a phase. Atomic position in a layer parallel to a(010) plane; out-of-plane oxygen atoms coordinated to the in-plane Li also shown. The full unit cell comprises two such layers, whose coordinates are related by inversion symmetry.

Fig. 4. Labels for Li sites in the high-Li (γ_b) phase. Atomic positions shown for a (010) layer; O (V) atoms denoted by circles (diamonds). The full unit cell comprises two such layers, whose coordinates are related by inversion symmetry.

Fig. 5. Calculated (histograms) and measured electrochemical potentials for $Li_{1+x}V_3O_8$.

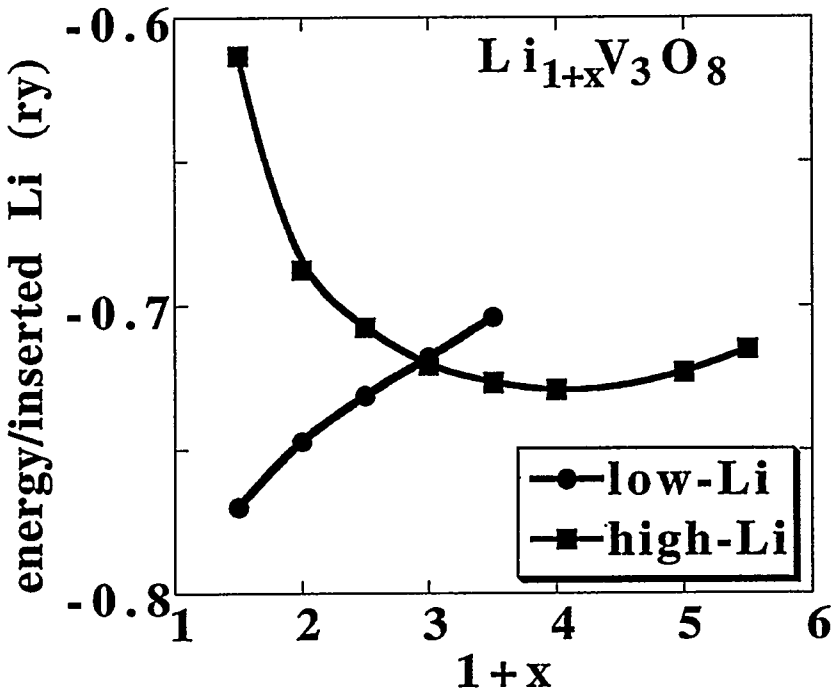
Li1+xV3O8
-0.6
-0.7
-0.8
energy/inserted Li (ry)
1
2
3
4
5
6
1+x
low-Li
high-Li

Figure 1

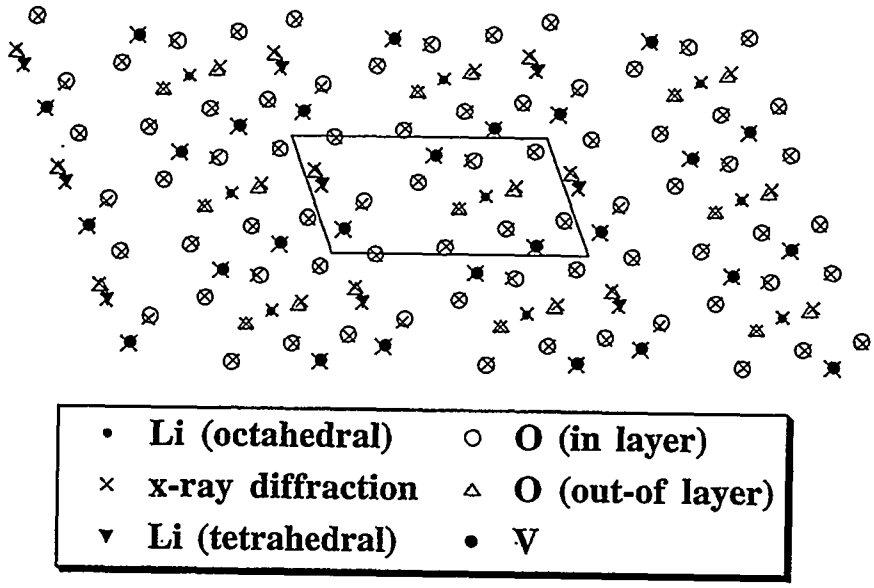
Li (octahedral)
x-ray diffraction
Li (tetrahedral)
O (in layer)
O (out-of layer)
V

Figure 2

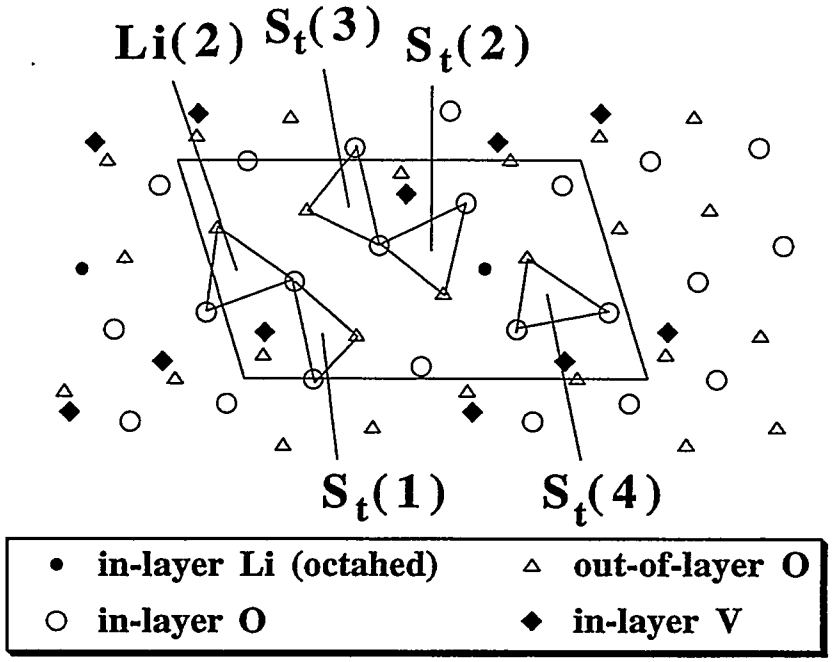
Li(2)
$S_t(3)$
$S_t(2)$
$S_t(1)$
$S_t(4)$
in-layer Li (octahed)
out-of-layer O
in-layer O
in-layer V

Figure 3

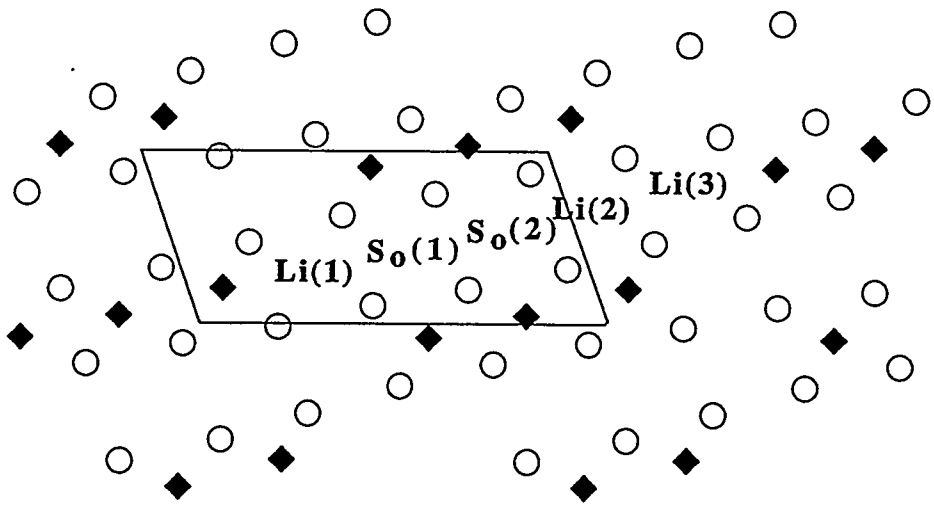

Figure 4

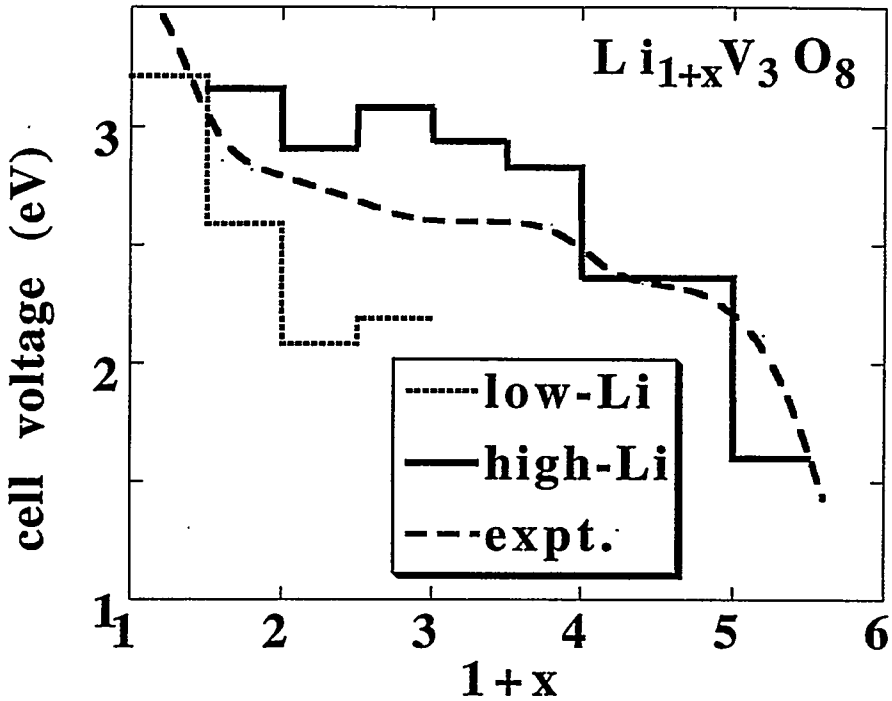

Figure 5