Can first principles calculations aid in lithium-ion battery design?

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Abstract

The possibility of calculating voltage curves for electrode materials in lithium-ion cells is introduced. These calculations rely on the use of modern high speed computers and require only the crystal structure of the host material as input. This means that voltage curves for new materials, which have not yet been synthesized, can in principle be calculated. This is by no means a replacement for experiments, but rather it could provide a systematic method for prioritizing a list of materials synthesis projects.

1. Introduction

The selection of suitable electrode materials for use in lithium-ion cells is of critical importance. A number of criteria must be considered including material cost, toxicity, rate capability, capacity, and voltage. This work is concerned with equilibrium voltage curves of electrode materials, which have a number of important properties that must be taken into account when designing a lithium-ion cell: (i) the average voltage; (ii) reversible capability; (iii) average slope; (iv) plateaus, and (v) other assorted features (Fig. 1).

The first two properties mentioned above are important for energy density considerations. Properties (iii) and (iv) must be considered when choosing the operating voltage range. For example, setting a trip point in the middle of a plateau is unwise. Other features can give significant insight as to the physical

Fig. 1. Parameters related to the operating voltage in the selection of suitable electrode materials.

processes taking place within the host material, such as ordered lithium super-lattice phases.

Lithium-ion electrode materials such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and various carbons are potential candidates for use in the first generation of lithium-ion cells. At present the search for second generation materials is intense. Many of these new materials involve atom substitutions or solid solutions such as $LiCo_zNi_{1-z}O_2$ [1], $LiNi_zFe_{1-z}O_2$[2], $LiMn_zM_{1-z}O_2$ [3], C_zB_{1-z} [4], C_zN_{1-z} [5]. Another approach is the synthesis of new materials such as $LT-LiMnO_2$ [6] and $LT-LiCoO_2$ [7]. Both are synthesized at low temperatures, and have new and interesting electrochemical properties.

Usually hundreds of man hours of experimental work are required to properly synthesize, characterize, and test the performance of a new material. This is also typically an iterative process. It is often necessary to prepare and characterize 10 to 100 samples in order to obtain a pure phase with promising performance in cells. The number of adjustable parameters (i.e., synthesis temperature, time, cooling rate, atmosphere, etc.), characterizing the synthesis conditions, is enormous. Also it is often difficult to guess in advance what the most important parameters are.

The object of this work is to point out, to workers in this field, that the technology now exists to calculate voltage curves of many materials, from first principles. Strictly speaking, first principles mean that no experimental input is required. The only information required are some fundamental laws of physics (namely quantum mechanics, and statistical thermodynamics) and the atomic numbers of all atoms in the host material and
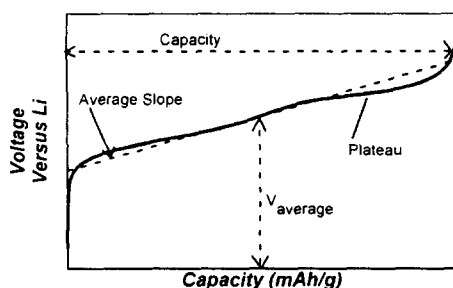
that of lithium. In practice, the calculator of voltage curves must also supply the crystal structure of the host material, which is always determined experimentally. The necessary fundamental laws of physics for such a calculation, have been known for almost 70 years. However, it is only recently with the proliferation of high speed computers, that it has been possible to routinely apply these laws to calculate physical properties of materials such as carbon and transition metal oxides.

Calculating voltage curves for lithium insertion materials is not new. Using lattice gas models with empirically chosen Li–Li and Li–host interactions, good agreement between model and experiment has been obtained for some systems. Below a lattice gas model will be explained, and how it is applied to calculate a voltage curve for $Li_xMo_6Se_8$ [8].

2. Lattice gas models

In a lattice gas model each lattice site, labelled i, is associated with a variable σ_i which takes on one of two values: $\sigma_i = 1$ if site i is occupied by Li and $\sigma_i = 0$ if the site is unoccupied. The goal is to express the energy of a configuration of Li atoms in terms of the σ_i variables, the Li–host binding energy, and any Li–Li interactions (repulsive or attractive). For example, if one site in the lattice is occupied:
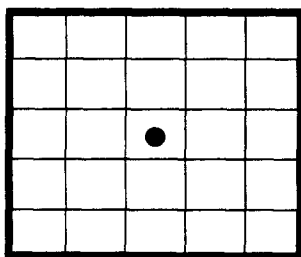
then the energy would be, J_1, which is the binding energy of one lithium atom to the host lattice. A numerical value will be assigned to J_1 below for the example where the host lattice is Mo_6Se_8. If two neighbouring cells are occupied:
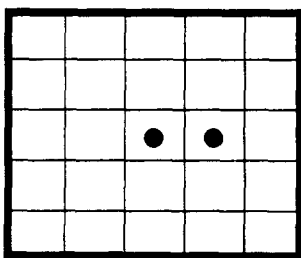
the lattice gas energy is, $2J_1 + J_2$, where J_2 is the near neighbour, pair interaction energy. Again a numerical value will be assigned to J_2 below. Of course, many

other possible interactions are possible, such are third and fourth neighbour interactions. These will not be considered here.

It is now straightforward to write down a general expression for the lattice gas energy:

$$Energy = J_1 \; \Sigma\sigma_i + J_2 \; 1/2\Sigma\sigma_i\sigma_j \tag{1}$$

which is valid for any configuration of lithium atoms.

Calculating a voltage curve, or for that matter any other thermodynamic quantity (i.e., heat capacity) from the energy expression above is basically an exercise in statistical thermodynamics. These techniques are now very well developed, and approximate calculations can be carried out by hand or in a matter of seconds on a desk-top computer, see Ref. [9].

Some numbers for the interactions J_1 and J_2 will be quoted, which depend on the details of the host material. For the Mo_6Se_8 host lattice, $J_1 = 2.07$ eV, $J_2 = -0.09$ eV (attractive) have been chosen. Why? These numbers are chosen so as to force the voltage curve calculated from the lattice gas model agree with the experimental voltage curve. One would then say that J_1 and J_2 have been determined empirically. The experimental and calculated voltage curves $V(x)$, and derivatives $-dx/dV$ for $Li_xMo_6Se_8$, are shown in Ref. [8]. The agreement is excellent.

If one is interested in calculating the voltage curve of $Li_xMo_6Se_8$ from first principles it will be necessary to calculate J_1 and J_2. To do this the concept of total energy has to be introduced.

3. Total energy

The total energy of an aggregate, which may be an atom, molecule or solid, is defined as the energy required to bring all constituent electrons and nuclei together from infinite distance (where they do not interact) to form the aggregate. Total energies are negative indicating that energy is gained upon forming an atom (molecule or solid) from its isolated constituents. Total energies can be calculated using the laws of quantum mechanics and require no experimental input. In the case of molecules and solids, the spatial arrangement of the atoms is required as input, and is considered as a statement of the problem to be solved, rather than as experimental data.

In the mid 1920s quantum mechanics was first developed. The total energy of the hydrogen atom (1 electron + 1 proton) was calculated (with pencil and paper) giving $E_{total} = -13.6$ eV. The next most complicated system is the helium atom (2 electrons + 1 nucleus) for which no exact solution exists, however approximate methods give $E_{total} = -79.0$ eV. It was not until the 1960s that it was possible to routinely treat simple diatomic molecules $Li_2 \rightarrow F_2$ with computers. Total energies for polyatomic molecules (3 to 10 atoms) were calculated by computer in the early 1970s.

Solid materials contain about 10^{23} atoms and it may appear that calculating the total energy of such a system from first principles would be impossible. However, the difficulty actually depends on the number of atoms in the primitive unit cell. Fortunately, many of the electrode materials which one is interested in ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and graphite) have rather simple unit cells. Also lots of fancy tricks and approximations have been developed over the years to further speed up the calculations of total energies of solids.

4. From total energies to interactions

Let us assume for the moment that one could calculate total energies for Mo_6Se_8 both without lithium and with some lithium residing in the lattice. How could one then determine the Li–host interaction J_1 and the Li–Li attraction J_2 used to model the voltage curve of $Li_xMo_6Se_8$? Let E_0 be the total energy of the empty Mo_6Se_8 lattice and E_1 be the energy of $Li_xMo_6Se_8$ with one lithium atom present (actually one lithium atom in each unit cell, where the unit cell is large enough that the lithium atoms do not interact significantly).

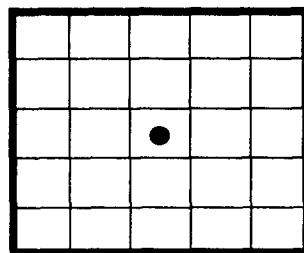Then it is easy to see that J_1 is just the difference between these two total energies:

$$J_1 = E_1 - E_0 \qquad (2)$$

To determine J_2 from first principles would require the calculation of one more total energy, that for a configuration with two lithium atoms situated next to each other, defined as E_2. With a little thought one finds that:
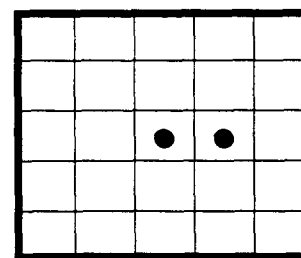
$$J_2 = E_2 - E_0 - 2J_1 \qquad (3)$$
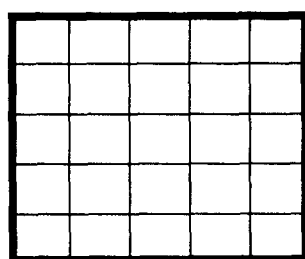
Total energy = E_0

Total energy = E_1

It takes some skill and experience to know which are the most important configurations for which one must calculate total energies. The author has not dealt with the problem of long range Li–Li interactions, which are far beyond the scope of this paper [8].

5. Li_yAl alloys

The voltage curve for a Li/Li_yAl cell has been calculated from first principles, (see Refs. [9] for details). In this case, total energies for five elementary configurations were used to calculate four distinct Li–host and Li–Li interactions. The statistical thermodynamics were then solved by computer using two methods to obtain the equilibrium voltage curve. The results are shown in Fig. 2 and compared with experiment. The comparison is slightly complicated by the large hysteresis observed in the experimental data, resulting from kinetic problems in nucleating the body centred cubic LiAl phase from the face-centred cubic Li_yAl phase. A small pseudo-plateau near $y = 1.1$ is due to the formation of another structure for which the total energy has not yet been calculated. Therefore, it is not presently possible to incorporate this feature into the calculation. This emphasizes the point made above that it is not trivial to decide which configurations and lattice structures are the most important.
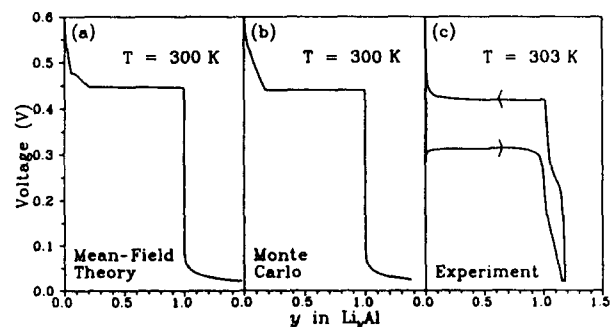
Total energy = E_2

Fig. 2. Voltage curves for Li_yAl using (a) and (b) first principles calculations, and (c) from experiment.
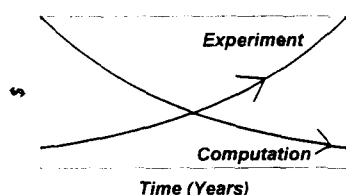
Fig. 3. Comparison of cost of computing and experimental approach.

6. What is next?

There are of course lots of things to do, the first of which would be to calculate voltage curves for well-known, relevant materials, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and graphite, in order gain some confidence in the methods. It would provide some fundamental understanding of why the voltage curves for these materials look the way they do. A minor modification would be to calculate voltage curves for solid solutions such as $LiMM'O_2$ materials where M and M' represent metal atoms such as Co, Ni, Mn, Cr, V, Fe, Cu, Al, Ti, etc. If any of these materials looks promising from first principles, then materials scientists would work a little harder synthesizing said material. The same holds for substitutions into carbon [4,5].

In this context, the first principles calculations would be used to screen candidate materials prior to synthesis. Experiment is by no means replaced, the calculations just provide a systematic approach to prioritizing materials synthesis projects.

7. Conclusions

If one believes that there are no more useful electrode materials to be discovered, then first principles calculations would seemingly serve no purpose. If on the other hand one believes that there are useful electrode materials just waiting to be discovered, then it seems clear that first principles calculations are another tool which can used to speed up the discovery process. As the cost of computing is always going down and the cost of experiment is on the rise, the calculational approach will be hard to ignore (Fig. 3). Computer simulations are, today, constantly used to test everything from microcircuit designs to aircraft wings, prior to assembling expensive prototypes. In all these situations it has of course taken time to gain confidence in the calculations.

It should be made clear that first principles calculations cannot yet deal with all materials. In particular disordered materials such as coke, are much more difficult to treat, basically because there is no unit cell which repeats itself, i.e., no periodic lattice. This makes total energies very difficult to calculate and the lattice gas model inapplicable as there is no lattice at all. Progress can be made in this area by studying the binding energy of lithium in quasi-disordered clusters of carbon atoms.

This sort of work is very multidisciplinary requiring state-of-the-art skills in condensed matter physics theory, statistical mechanics, electrochemistry, chemistry, and lithium-ion technology. It will be interesting to see if the scientist can break down the arbitrary boundaries which currently seem to isolate these various disciplines.

References

[1] C. Delmas and I. Saadoune, *Solid State Ionics, 53–56* (1992) 370; T. Ohzuku, H. Komori, K. Sawai and T. Hirai, *Chem. Express, 5* (1990) 733; J.N. Reimers, J.R. Dahn and U. von Sacken, *J. Electrochem. Soc., 140* (1993) 2752.

[2] J.N. Reimers, E. Rossen, C.D. Jones and J.R. Dahn, *Solid State Ionics, 61* (1993) 335.

[3] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon and S. Colson, *J. Electrochem. Soc., 138* (1991) 2859.

[4] M. Morita et al., *J. Electrochem. Soc., 139* (1992) 1227; B.M. Way and J.R. Dahn, *J. Electrochem. Soc., 141* (1994) 907, and refs. therein.

[5] W.J. Weydanz, B.M. Way, T. van Buuren and J.R. Dahn, *J. Electrochem. Soc., 141* (1994) 900.

[6] T. Ohzuku, A. Ueda and T. Hirai, *Chem. Express, 7* (1992) 103; J.N. Reimers, E.W. Fuller, E. Rossen and J.R. Dahn, *J. Electrochem. Soc., 140* (1993) 3396.

[7] R.J. Gummow, M.M. Thackery, W.I.F. David and S. Hull, *Mater. Res. Bull., 27* (1992) 327; R. Rossen, J.N. Reimers and J.R. Dahn, *Solid State Ionics, 62* (1993) 53.

[8] J.R. Dahn and W.R. McKinnon, *Phys. Rev. B, 31* (1984) 484; S.T. Coleman, W.R. McKinnon and J.R. Dahn, *Phys. Rev. B, 29* (1984) 4147.

[9] J.N. Reimers and J.R. Dahn, *Phys. Rev. B, 47* (1993) 2995, and refs. therein.