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Calculated cell discharge curve for lithium batteries with a V_2O_5 cathode

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Electronic structure techniques now enable accurate estimates of cell voltages of solid state batteries employing intercalation cathodes: we calculate the variation of cell potential with the degree of discharge—a crucial factor determining the applicability and utility of cathode materials—for the $Li_xV_2O_5$ cathode system.

Lithium batteries are of growing technological importance with applications in mobile telephones and laptop computers. Most current systems comprise a lithium anode (which may be lithium metal or, more commonly, a lithium graphite bronze) with the cathode being a transition metal oxide or sulfide into which lithium intercalates reversibly. The electrolyte is usually an organic polymer with high ionic conductivity.[1] A wide range of cathode materials have been investigated experimentally, including CoO_2[2] and $LiMn_2O_4$.[3,4] In this paper we present, to our knowledge, the first application of first principles electronic structure techniques to the prediction of discharge voltage curves for this type of battery system.

Clearly, the cell voltage, V, depends on the free energy of the intercalation reaction, which, for the V_2O_5 system on which we concentrate in this paper, can be written as:

$$x\mathrm{Li}_{(s)} + V_2O_5 \Rightarrow \mathrm{Li}_xV_2O_5 \qquad (1)$$

where by $\mathrm{Li}_{(s)}$ we indicate metallic lithium.

The EMF is obtained from the partial molar free energy, ΔG, of reaction 1 using the Nernst relationship. In this study, we approximate ΔG by the internal energy term, ΔE, since the contributions of the vibrational and configurational entropy terms to the cell voltage at room temperature are expected to be small (<0.1 V). To estimate the internal energy we calculate the energy, $E(x)$, of a number of $Li_xV_2O_5$ phases and of lithium metal, $E(\mathrm{Li})$, and then use the finite difference approximation:

$$\Delta E(x') = \{E(x_2) - [E(x_1) + (x_2 - x_1)E(\mathrm{Li})]\}/(x_2 - x_1) \qquad (2)$$

where $x_2 > x_1$ and $x' = 1/2(x_1 + x_2)$. It should be stressed that $\Delta E(x')$ leads to a predicted cell voltage that is an average value for all $Li_xV_2O_5$ compositions between x_1 and x_2. Also, the number of configurations, and therefore, the resolution of the calculated voltage curve, is limited by the size of the simulation cell that it is possible to use.

Earlier studies[5] have predicted single values for the average discharge voltage between two compositions that have often been significantly different in terms of their lithium content. While these studies showed that theoretical techniques could be used with great success to predict cell voltages and make basic comparisons between different transition metal oxide systems, there has been no attempt to model, in detail, the dependence of the cell voltage, E, on the lithium concentration, x, in a single cathode material. Often this relationship is a complex one which reflects the changing lithium environment within the cathode host, and produces a discharge curve with relatively flat plateaux separated by well defined steps.

To calculate the internal energy of each configuration we use periodic boundary conditions within the framework of gradient-corrected density functional theory (DFT) techniques, employing the VASP[6–8] code. This method solves the Kohn–Sham equations[9,10] to obtain a self-consistent, valence shell electron density within the non-local field of the ultra-soft psuedopotential[11,12] representation of the nuclei and the core electrons. Details of the method and its implementation for the case of $Li_xV_2O_5$ were presented by Braithwaite *et al.*,[13] which also demonstrates the reliability of the method for modelling this system. The calculations use a plane wave basis set with a kinetic energy cutoff of 550 eV, which has been shown to be adequate for the purpose of calculating the ΔE of reaction 1.[13] All calculations involve full geometry optimisation which, as shown previously,[13] reproduces accurately the structure of V_2O_5, shown in Fig. 1.

Six values of x in $Li_xV_2O_5$ were studied by setting up supercells of composition $x = 0.25$, 0.5, 0.75, 1.0, 1.5, and 2.0. The lithium atoms were inserted in the channel that runs along the 010 direction, (Fig. 1), which has been shown, by interatomic potential based defect calculations, to be the most stable site for intercalated Li^+ ions. The results are summarised in Table 1, while calculated and experimental data are compared in Fig. 2.

The results reveal a good measure of agreement between the calculated and experimental data. There is a systematic underestimation of the experimental voltages, which has also been seen by other authors,[5] and is probably due to an overestimation of the binding energy of lithium metal. However, the variation of $E(x)$ with x is generally well reproduced over a wide range of compositions. The most important feature of the experimental curve is the step at

Table 1 Compositions and calculated internal energies used in the cell voltage calculation. Compositions refer to the formula of the full unit cell used in the simulations

Composition	Internal energy $E(x)$/eV
$\mathrm{Li}_{(s)}$	−1.903
V_8O_{20}	−236.321
$Li_1V_8O_{20}$	−241.359
$Li_2V_8O_{20}$	−246.343
$Li_3V_8O_{20}$	−250.910
$Li_4V_8O_{20}$	−255.446
$Li_6V_8O_{20}$	−261.964
$Li_8V_8O_{20}$	−269.001

around $x = 0.8–0.9$, which we consider is acceptably reproduced in the calculated data given the limitations of the restricted number of simulations. The minimum at $x = 1.25$ is an artefact which almost certainly arises from the limited number of compositions that it is possible to simulate. This factor has the greatest affect on the accuracy of the calculated voltage for compositions where there is a rapid variation of E with x. Future work will aim to achieve better resolution in the region of the curve around $x = 1.0$.

Since the variation of the cell voltage with lithium concentration, x, is controlled by a complex interplay of electronic factors, it is gratifying that calculation and experiment are, on the whole, in such close agreement. Our results suggest that this type of calculation may be used to model accurately the electrochemical properties of cathode materials for use in solid-state batteries.

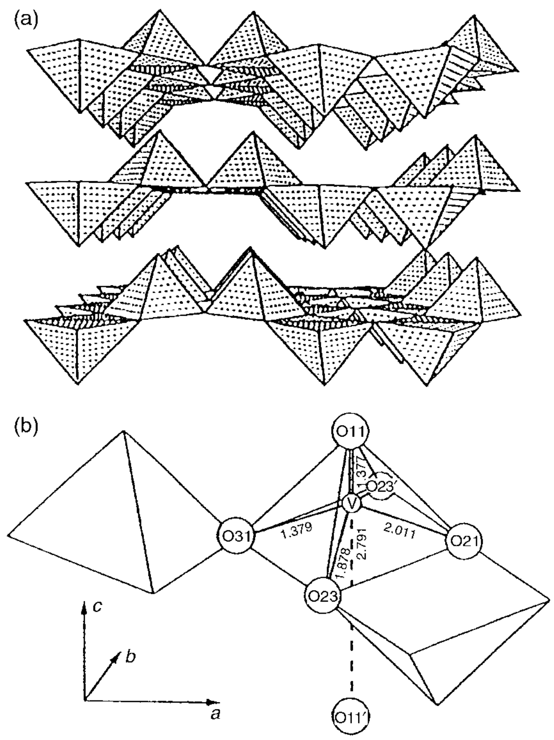

Fig. 1 V_2O_5 structure as VO_5 square-based pyramidial units: (a) layers looking along the 010 direction; (b) co-ordination around the vanadium.[14]

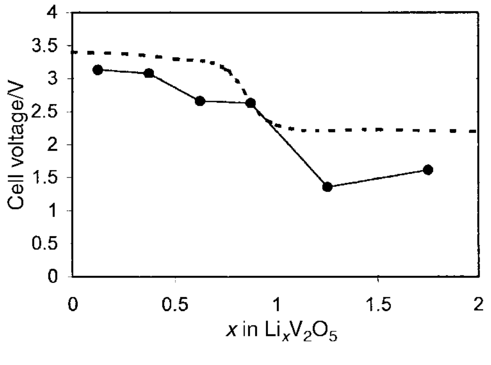

Fig. 2 Calculated (solid) and experimental[15] (dashed) voltage curves for $Li_xV_2O_5$.

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