



Ab initio calculation of the voltage profile for LiC_6

K.R. Kganyago^{a,*}, P.E. Ngoepe^{a,b}, C.R.A. Catlow^c

^aMaterials Modelling Center, School of Physical and Mineral Sciences, University of the North,
P/Bag X 1106, Sovenga, 0727, South Africa

^bManufacturing and Materials Technology, Council for the Scientific and Industrial Research, Pretoria, 0001, South Africa

^cDavy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, UK

Received 12 March 2002; received in revised form 10 June 2002; accepted 29 July 2002

Abstract

Energetics of the anode system LiC_6 compared to metallic lithium are calculated within the framework of local-density functional theory (LDA-DFT) techniques. Our results suggest that the energy of anode intercalation results in a small change to the cell voltage.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 71.15.–m

Keywords: Density functional theory; LiC_6 ; Cell voltage

1. Introduction

Lithium-ion batteries [1–3] are the current and widely used rechargeable power source for portable electronics devices because of their high energy density. Previous theoretical studies [4–8] have modelled the energetics and corresponding cell voltage curves of the cathode materials. Aydinol et al. [5] calculated the average voltages for Li/LiMO_2 and Li/LiCoX_2 ($M = \text{Ti}, \text{V}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Al}$; $X = \text{O}, \text{S}, \text{Se}$) cells. An approximation made in these calculations is that the transformation from reactant to product is in two phases, so an average voltage can be defined [5]. Courtney et al. [6] used the ab initio pseudopotential plane-wave method and the approximation by Aydinol et al. [5] to calculate the

average voltage for the anode material tin-oxide (in particular, lithium–tin, Li_xSn_y). Deiss et al. [4] calculated the energy density and cell voltages of $\text{LiC}_6/\text{LiMoO}_2$ (anode/cathode) and $\text{LiC}_6/\text{NiO}_2$ using the average voltage between the fully charged and the discharged states. Yamaki et al. [7] studied the contribution of the internal energy change to cathode voltage assuming that the cathode material (NiO_2) is completely ionic and only the Coulombic potential was effective. Braithwaite et al. [8] used the ab initio pseudopotential plane-wave method and the finite difference approximation to calculate the variation of the cell potential with the degree of discharge. These calculations establish the value and reliability of DFT techniques in modelling the energetics of intercalation. It is the purpose of this communication to apply the same method to the problem of the anode intercalation reaction which has not previously been studied.

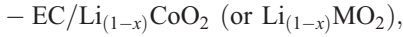
* Corresponding author. Fax: +27-152683268.

E-mail address: khomotso@technologist.com (K.R. Kganyago).

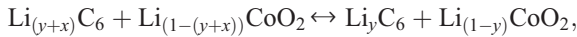
2. Li battery system

The basic cell structure of the lithium battery is of the type

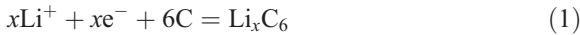
$\text{Li}_x\text{C}_6/\text{LiX}$ in PC



where LiX is a lithium salt (e.g. LiClO_4), PC–EC is a mixed propylene carbonate (PC)–ethylene carbonate (EC) solvent and M is a transition metal (e.g. Ni, Mn or Co). The electrochemical process is as follows



where y is about 0.2 Faraday per mole and the cyclable charge x is around 0.5 [1]. The anode reaction can be summarised as:



In this communication, we explore the contribution to the voltage by the anode material using first-principles electronic structure techniques. We focus our attention to Li_xC_6 ($x=0$ and 1) where the latter, the so-called 1st stage lithium intercalated graphite, is the experimentally reported [9] anode configuration.

3. Theoretical method

The total energy (E^{tot}) code CASTEP [10] was used, which employs pseudopotentials to describe electron–ion interactions and represents the electronic wavefunction using a plane-wave basis set [11]. The total energy is calculated within the framework of the local-density approximation (LDA) for the exchange–correlation energy. We chose LDA rather than the gradient generalized approximation (GGA) because the associated carbon pseudopotentials describe the interaction between graphite planes better than the GGA carbon pseudopotentials [12–14]. Energy cutoffs of up to 900 eV were used for the expansion of the wave functions where a single point sampling of the Brillouin zone produced converged results in the Fourier space [15]. The interactions between the ionic cores and the electrons are described by norm-conserving pseudopoten-

tentials [16]. The pseudo-wave functions, the smooth part of the charge density and the potential are represented on a fast-Fourier transforms (FFT) grid of $16 \times 16 \times 16$, $18 \times 18 \times 50$ and $32 \times 32 \times 27$ for metallic lithium (Li_{metal}), graphite and LiC_6 , respectively. These minimum FFT grids applied to the exchange–correlation potential ($V_{\text{xc}}(G-G')$) are sufficient for the cutoff energies. Li_{metal} used 26 sampling k -points in the irreducible wedge of the Brillouin zone. For the calculation in space group $\text{P6}_3/\text{mmc}$ (graphite) and $\text{P6}/\text{mmm}$ (LiC_6), 24 and 15 sampling k -points in the irreducible Γ wedge of the Brillouin zone were used, respectively. The k -points were generated with the Monkhorst–Pack [17] scheme with parameters ($8 \times 8 \times 8$), ($9 \times 9 \times 4$) and ($5 \times 5 \times 6$) for Li_{metal} , graphite and LiC_6 , respectively. Each k -point was represented with an equivalent of 540, 3650 and 3200 plane-waves for Li_{metal} , graphite and LiC_6 , respectively. All calculations involve full geometry optimization of Li_{metal} , graphite and LiC_6 with the total energy fully converged with respect to k -point and energy cutoff. Geometry optimization at zero pressure was performed with the variable lattice parameter and full relaxation of the internal coordinates. Calculations were considered to be convergent when the maximum force on an atom was below $0.01 \text{ eV } \text{\AA}^{-1}$.

4. Results

The total energy calculations for graphite, lithium metal and LiC_6 are reported in Table 1. LiC_6 contains six carbon atoms per unit cell and graphite contains four. Therefore, to obtain ΔE for the intercalation reaction, we write:

$$E_{\text{LiC}_6}^{\text{tot}} - \left(\frac{3}{2}E_{\text{graphite}}^{\text{tot}} + E_{\text{Li}_{\text{metal}}}^{\text{tot}}\right) = \Delta E \quad (2)$$

Using the values given in the Table 1, we obtain a value of -0.145 eV for ΔE . This result can be

Table 1
Calculated E^{tot} for C, Li_{metal} and LiC_6 systems

	LiC_6	C	Li_{metal}
E^{tot} (eV)	– 940.30	– 621.93	– 7.26

compared with experimental data of Avdeev et al. [9], who report a value of 0.145 eV (-13.9 ± 1.2 kJ/mol) per Li for the intercalation of Li from the liquid phase into graphite; when corrected for the heat of fusion of lithium, we obtain 0.175 eV which compares well with our calculated value.

The small negative values accord qualitatively with experiment and suggest that the use of graphite/Li anode compound instead of pure Lithium will only result in a small change of about 5% to the cell voltage. Such calculations may now clearly be used routinely to determine the contributions of the anode and cathode processes to the cell voltage.

Acknowledgements

We would like to acknowledge the National Research Foundation (NRF) and Royal Society (UK) for financial support of the execution of this work. We are also grateful to the Materials Modelling Center for the availability of computational facilities at the University of the North.

References

- [1] T. Naguara, K. Takazawa, *Prog. Batteries Sol. Cells* 9 (1990) 20.
- [2] K. Brandt, *Solid State Ionics* 69 (1994) 173.
- [3] Y. Nishi, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Kodansha and Wiley-VCH, Tokyo (Japan), 1998, Chap. 8.
- [4] E. Deiss, A. Wokaun, J.L. Barass, C. Daul, P. Dufek, *J. Electrochem. Soc.* 144 (1997) 3877.
- [5] M.K. Aydinol, A.F. Kohan, G. Ceder, K. Cho, J. Joannopoulos, *Phys. Rev. B* 56 (1997) 1354.
- [6] I.A. Courtney, J.S. Tse, O.U. Mao, J. Hafner, J.R. Dahn, *Phys. Rev. B* 58 (1998) 15583.
- [7] J. Yamaki, M. Egashira, S. Okada, *J. Power Sources* 90 (2000) 116.
- [8] J.S. Braithwaite, C.R.A. Catlow, J.D. Gale, J.H. Harding, P.E. Ngoepe, *J. Mater. Chem.* 10 (2000) 239.
- [9] V.V. Avdeev, A.V. Savchenkova, L.A. Monyakina, I.V. Nikol'skaya, A.V. Khvostov, *J. Phys. Chem. Solids* 57 (1996) 947.
- [10] V. Milman, B. Winkler, J.A. White, C.J. Pickard, M.C. Payne, E.V. Akhmatkaya, R.H. Nobes, *Int. J. Quantum Chem.* 77 (2000) 895.
- [11] M.C. Payne, M.P. Teter, D.C. Allan, J.D. Joannopoulos, *Rev. Mod. Phys.* 64 (1992) 1045 (and references therein).
- [12] G. Kern, J. Hafner, *Phys. Rev. B* 58 (1998) 13167.
- [13] K.R. Kganyago, P.E. Ngoepe, *Mol. Simul.* 22 (1999) 39.
- [14] J.V. Badding, T.J. Scheidemantel, *Solid State Commun.* 122 (2002) 473.
- [15] K.R. Kganyago, MSc Dissertation, Chapter 3 (2000).
- [16] J.S. Lin, A. Qteish, M.C. Payne, V. Heine, *Phys. Rev. B* 47 (1993) 4174.
- [17] H.J. Monkhorst, J.D. Pack, *Phys. Rev.* 13 (1976) 5188.