A Theoretical Study of Alkali Metal Intercalated Layered Metal Dichalcogenides and Chevrel Phase Molybdenum Chalcogenides.

By:

Khomotso R Kganyago

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Supervisor: Professor P. E. Ngoepe

Co-Supervisor: Professor C. R. A. Catlow

Declaration

I declare that the dissertation hereby submitted to the University of the North for the degree of Doctor of Philosophy has not been previously submitted by me for a degree at this or any other university, that it is my own work in design and in execution, and that all material contained therein has been duly acknowledged.

Signature of the Author: ……………………………………………………….
Khomotso R. Kganyago

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TO MY PARENTS

PHUTI AND RAMOKONE

MY WIFE

LEBOHANG

AND MY SONS

PHUTI AND MAGATA

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Abstract

This thesis explores the important issues associated with the insertion of Mg^{2+} and Li^{+} into the solid materials: molybdenum sulphide and titanium disulphide. This process, which is also known as intercalation, is driven by charge transfer and is the basic cell reaction of advanced batteries. We perform a systematic computational investigation of the new Chevrel phase, $Mg_xMo_6S_8$ for $0 \le x \le 2$, a candidate for high energy density cathode in prototype rechargeable magnesium (Mg) battery systems. Mg^{2+} intercalation property of the Mo_6S_8 Chevrel phase compound and accompanied structural changes were evaluated. We conduct our study within the framework of both the local-density functional theory and the generalised gradient approximation techniques. Analysis of the calculated energetics for different magnesium positions and composition suggest a triclinic structure of $Mg_xMo_6S_8$ ($x = 1$ and 2). The results compare favourably with experimental data. Band-structure calculations imply the existence of an energy gap located ~1 eV above the Fermi level, which is a characteristic feature of the electronic structure of the Chevrel compounds. Calculations of electronic charge density suggest a charge transfer from Mg to the Mo_6S_8 cluster, which has a significant effect on the Mo-Mo bond length.

There is relatively no theoretical work, in particular *ab initio* pseudopotential calculations, reported in literature on structural stability, cations "site energy" calculations, and pressure work. Structures obtained on the basis from experimental studies of other ternary molybdenum sulphides are examined with respect to pressure-induced structural transformation. We report the first bulk and linear moduli of the new Chevrel phase structures.

This thesis also studies the reaction between lithium and titanium disulfide, which is the perfect intercalation reaction, with the product having the same structure over the range of reaction $0 \le x \le 1$ in Li_xTiS_2. Calculated lattice parameters, bulk moduli, linear moduli, elastic constants, density of states, and Mulliken populations are reported.
Our calculations confirm that there is a single phase present with an expansion of the crystalline lattice as is typical for a solid solution, about 10% perpendicular to the basal plane layers. A slight expansion of the lattice in the basal plane is also observed due to the electron density increasing on the sulfur ions. Details on the correlation between the electronic structure and the energetic (i.e. the thermodynamics) of intercalation are obtained by establishing the connection between the charge transfer and lithium intercalation into TiS_2. The theoretical determination of the densities of states for the pure TiS_2 and Li_1TiS_2 confirms a charge transfer. Lithium charge is donated to the S (*3p*) and Ti (*3d*) orbitals. Comparison with experiment shows that the calculated optical properties for energies below 12 eV agrees well with reflectivity spectra.

The structural and electronic properties of the intercalation compound Li_xTiS_2, for x = 1/4, 3/4, and 1, are also investigated. This study indicates that the following physical changes in Li_xTiS_2 are induced by intercalation: (1) the crystal expands uniaxially in the *c*-direction, (2) no staging is observed. We also focus on the intercalation voltage where the variation of the cell potential with the degree of discharge for $LiTiS_2$ is calculated. Our results show that it can be predicted with these well-developed total energy methods.

The detailed understanding of the electronic structure of the intercalation compounds provided by this method gives an approach to the interpretation of the voltage composition profiles of electrode materials, and may now clearly be used routinely to determine the contributions of the anode and cathode processes to the cell voltage. Hence becoming an important tool in the selection and design of new systems.

Keywords

Magnesium rechargeable battery; Chevrel, Lithium batteries; Li and Mg-ion insertion; TiS_2; Mo_6S_8; Charge transfer; reflectivity, intercalation, elastic constants, voltage, EOS, Moduli.