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Intercalation Voltages for Spinel LixMn2O4 (0≤x≤2) Cathode Materials: Calibration of Calculations with the ONETEP Linear-Scaling DFT Code

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Abstract:	Density functional theory (DFT) has become an engine for driving ab-initio quantum mechanical simulations spanning a vast range of applications. However, conventional DFT has limitations of the accessible system size due to computational expense. Recent progress on linear scaling DFT methods has enabled us to investigate larger systems. In this paper, we investigate the numerical agreement between conventional DFT codes and ONETEP, a linear-scaling DFT code, for important materials properties particularly calculating the intercalation potential of spinel electrode materials. Modulating materials with high energy density is an important aspect that contributes to the significant gap in our knowledge of the factors. We provide typical simulation results based on calculated intercalation potentials for discharging the spinel Li x Mn 2 O 4 , which plays a key role in developing high energy density lithium-ion batteries. The structural properties obtained after geometry optimisation with CASTEP yielded materials with volume within 3% and lattice parameters within 1% relative error with experimental values. The average intercalation potentials calculated with the CASTEP and ONETEP codes are within 3% agreement with each other.
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Tackling energy storage challenges through computational simulations has proven to be one of the most effective ways to diagnose and analyse battery issues at multi-scales. Modulating materials with high energy density is an important aspect that contributes to the significant gap in our knowledge of the factors. Density functional theory (DFT) has become an engine for driving ab-initio quantum mechanical simulations spanning a vast range of applications. However, conventional DFT has limitations of the accessible system size due to computational expense. As such, recent interest is driven towards utilisation of linear-scaling methods for DFT simulations in a quests to exploit the predictive power of DFT calculations on larger systems. This capability of ONETEP code allows the unique extension of DFT studies to larger systems simulated spontaneously using molecular dynamics methods.

The average intercalation potentials at which Li can be inserted into the various structures have been investigated owing to the recent progress on linear scaling DFT methods. In the current study, we explore accuracy of the ONETEP linear-scaling DFT code for the study of Li-insertion in spinel electrode material and benchmarking its results with those of the conventional DFT CASTEP code. This is done by investigating the numerical agreement between conventional DFT codes and ONETEP, a linear-scaling DFT code. We provide typical simulation results based on calculated intercalation potentials for discharging the spinel $Li_xMn_2O_4$, which plays a key role in developing high energy density lithium-ion batteries. The structural properties obtained after geometry optimisation with CASTEP yielded materials with volume within 3 % and lattice parameters within 1 % relative error with experimental values. The average intercalation potentials calculated with the CASTEP and ONETEP codes are within 3 % agreement with each other.

The findings of this study demonstrate the viability to perform reliable and coherent linear-scaling DFT calculations for metallic systems. It is further envisaged that the approach will be employed in calculations of voltage profiles for larger lithium ion battery electrodes nano-architectures (nanoparticles, nanorods, nanosheets and nanoporous structures) consisting of more than 3000 atoms, which have been generated spontaneously by simulated amorphization recrystallization methods, where classical force fields were invoked. In conclusion, our work, is an ongoing effort of assembling modelling tools, across length scales, that will enable us to shed valuable insights on destructive structural changes contributing to Li-ion battery capacity fade and failure during repeated charging and discharging.

With kind regards,

Dr Raesibe Ledwaba

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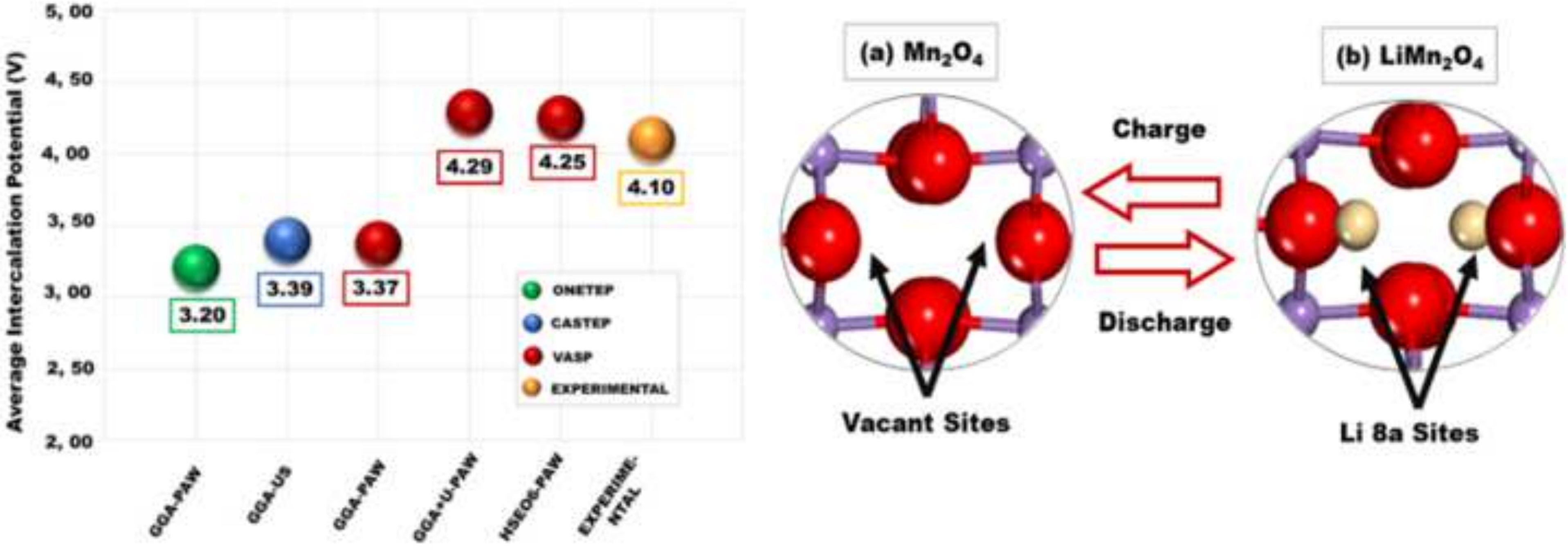
Average Intercalation Potential (V)
5, 00
4, 50
4, 00
3, 50
3, 00
2, 50
2, 00
3.20
3.39
3.37
4.29
4.25
4.10
● ONETEP
● CASTEP
● VASP
● EXPERIMENTAL
GGA-PAW
GGA-US
GGA-PAW
GGA+U-PAW
HSE06-PAW
EXPERIME-NTAL
(a) Mn_2O_4
(b) $LiMn_2O_4$
Charge
Discharge
Vacant Sites
Li 8a Sites

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Intercalation Voltages for Spinel $Li_xMn_2O_4$ ($0 \leq x \leq 2$) Cathode Materials: Calibration of Calculations with the ONETEP Linear-Scaling DFT Code

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Abstract: Density functional theory (DFT) has become an engine for driving ab-initio quantum mechanical simulations spanning a vast range of applications. However, conventional DFT has limitations of the accessible system size due to computational expense. Recent progress on linear scaling DFT methods has enabled us to investigate larger systems. In this paper, we investigate the numerical agreement between conventional DFT codes and ONETEP, a linear-scaling DFT code, for important materials properties particularly calculating the intercalation potential of spinel electrode materials. Modulating materials with high energy density is an important aspect that contributes to the significant gap in our knowledge of the factors. We provide typical simulation results based on calculated intercalation potentials for discharging the spinel $Li_xMn_2O_4$, which plays a key role in developing high energy density lithium-ion batteries. The structural properties obtained after geometry optimisation with CASTEP yielded materials with volume within 3 % and lattice parameters within 1 % relative error with experimental values. The average intercalation potentials calculated with the CASTEP and ONETEP codes are within 3 % agreement with each other.

Keywords: Intercalation Potential, Performance, Spinel, Linear-Scaling DFT, Cycling, DFT

1. Introduction

Pioneering research has been carried out over the years for developing electrode materials with high specific capacity, enhanced cycling stability, and high rate capability in electrode materials for lithium-ion batteries. This interest is driven by the urgent need to manufacture energy storage materials (batteries) that deliver high energy density for a broad range of

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applications i.e. from mobile devices to electric vehicles (EVs) as well as large scale smart grids for power utilities [1, 2, 3]. Spinel $LiMn_2O_4$ and its derivatives have drawn significant interest as potential cathodes lithium batteries owing to its cubic structure that capacitates three-dimensional diffusion paths, to deliver capacity approximately 140 mAh g^{-1} [4]. The utilisation of spinel $LiMn_2O_4$ (LMO) would be beneficial considering its high Li intercalation voltage range of 3.0 – 4.3 V, which contributes to delivery of the high energy density [5]. Despite these excellent properties, the LMO cathode has been reported to suffer from severe capacity fading [3], which presumably emanates from structural complexities due to multiple valences of Mn, which accelerate occurance of Jahn-Teller effect and resultant Mn dissolution during cycling [6]. It is imperative to devise means to enhance cycling stability of LMO by lowering the Mn^{3+} content and enhancing the strength of Mn-O bonds [3], since this capacity decay affects the operating voltage of the LMO electrode, and subsequently the overall efficiency of the battery [1]. The maximum energy attainable by the battery depends strongly on the by-product voltage and capacity of the cathode and anode material [7]. This presents an opportunity to explore routes to improved energy density in through better understanding of the factors influencing the electrochemical potential.

Future designs of suitable electrode materials with high energy density rely on development of batteries operating in a higher voltage window than currently attainable ideally one with a higher-potential cathode and a lower-potential anode. The redox potential attained during the reaction governs the energy at which the battery operates. Oxidization of metallic lithium takes occurs on the anode of the rechargeable battery and the Li-ion is then intercalated into the cathode material comprised of a transition metal compound during the discharge cycle., thus yielding high redox potential [1, 8, 9]. This ignites significant interest to explore new research avenues for understanding rules and origins of electrochemical potential are crucial for modification of superior electrode with high operating voltage.

Various methods have been used in a quest to enhance the cycle stability of lithium ion batteries during which the electrochemical performance was calculated and analysed across electronic structure and atomistic simulation methods [1]. First principles calculations have had an immense impact on how material properties are studied, particularly for the extensive usage in prediction of intercalation dependent variables such as the stability of material phases, voltage profile [8, 10]. Despite this success, computational costs of this technique limits the

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accessible system size as per number of atoms [8]. The recent emergence of linear-scaling methods [11] gives us the capability to perform cost-effective DFT calculations, wherein the computational cost increases linearly as the number of atoms within the system is increased, and with no significant loss in accuracy as recently demonstrated for metallic systems [12, 13].

Linear-scaling methods are typically more complicated to implement than conventional methods but can take full advantage of parallel computing [14]. As such, recent interest in is driven towards utilisation of linear-scaling methods for DFT simulations in a quests to exploit the predictive power of DFT calculations on larger systems. This capability of ONETEP code [15] will allow the unique extension of DFT studies to larger systems simulated spontaneously using molecular dynamics methods [16]. In the current study, we explore accuracy of the ONETEP linear-scaling DFT code for the study of Li-insertion in spinel electrode material and benchmarking its results with those of the conventional DFT CASTEP code [17]. The average intercalation potentials at which Li can be inserted into the various structures will be investigated.

2. Method

In this section, we discuss briefly, the computational details for simulating the spinel $Li_xMn_2O_4$, the codes used to carry out the electronic structure calculations, details on the structural optimisation process of models and calculation of average intercalation potentials during the discharge process.

2.1. Models

The conventional unit cell comprises of two formula units in the face centred cubic structure spinel Mn_2O_4 (a), where a series of intersecting tunnels form in the Mn_2O_4 host structure by the face-sharing of tetrahedral lithium (8a) sites and vacant octahedral (16c) sites in edge-shared octahedral. The Mn atoms occupy half of the octahedral (16d) sites in an intervening cubic close-packed formation of oxygen atoms at 32e sites [18, 19] allowing for insertion/removal of lithiums within the $LiMn_2O_4$ cathode material. Diffusion of Li-ions is facilitated through migration between the tetrahedral (8a) sites via the octahedral (16c) sites as demonstrated in figure 1 (a-c). The movement of Li-ions in the spinel structure occurs along the 3D-pathways through a zig-zag motion [20].

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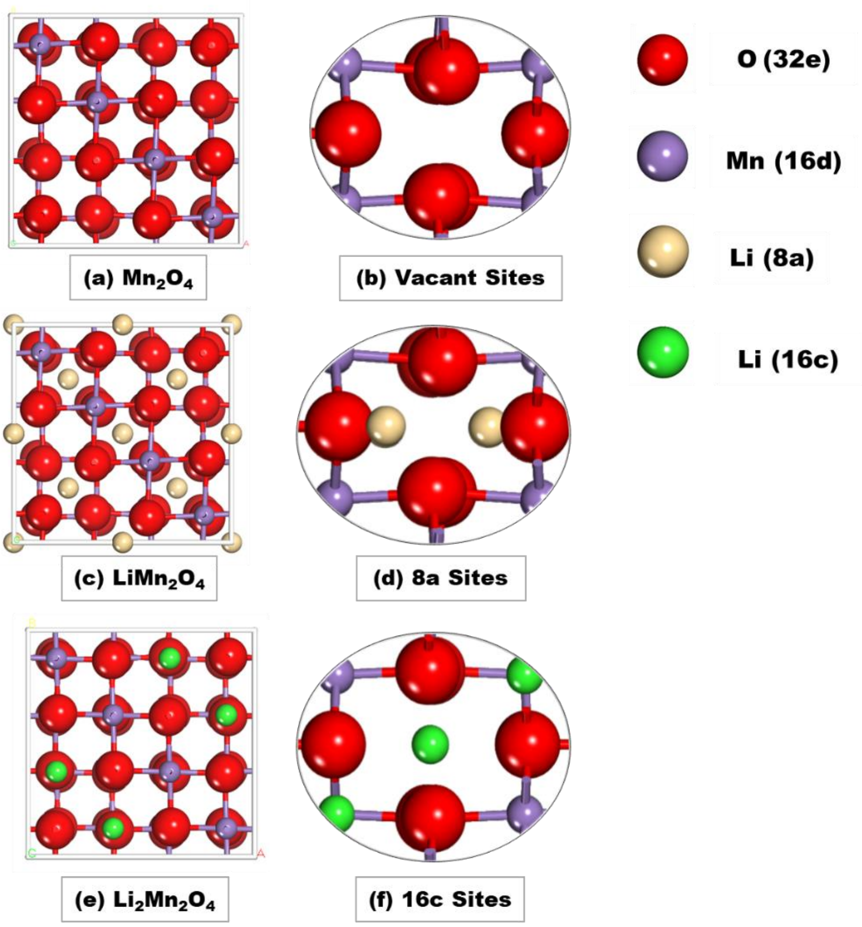

Figure 1: Crystallographic structures of the spinel $Li_xMn_2O_4$ ($0 \leq x \leq 2$) demonstrating conventional unit cells of (a) Mn_2O_4, (c) $LiMn_2O_4$ and (e) $Li_2Mn_2O_4$, together with their intercalation sites denoted as; (b) vacant, (d) 8a, (f) 16c, respectively.

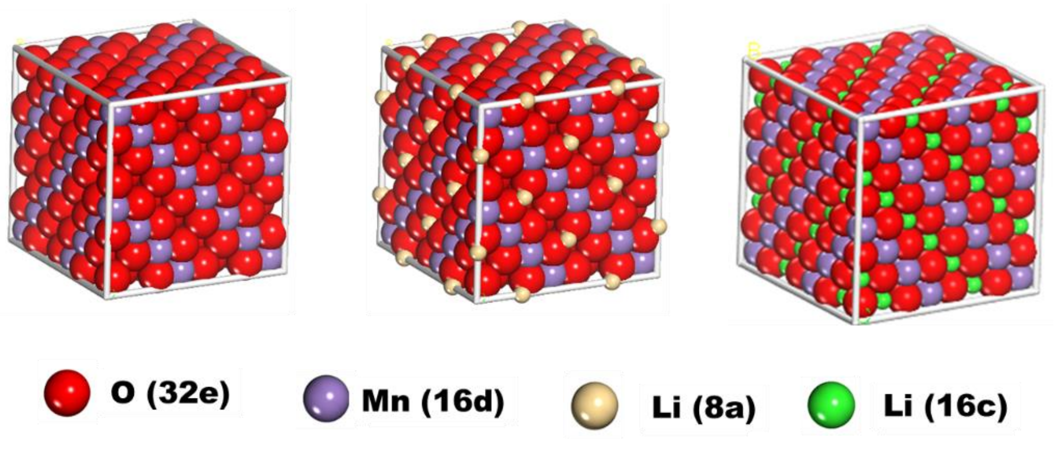

Figure 2: Models for 2x2x2 supercells structures of $Li_xMn_2O_4$ ($0 \leq x \leq 2$).

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2.2.Computational Details

Structural relaxation calculations for all spinel $Li_xMn_2O_4$ systems were performed by fully optimising their atomic positions and lattice parameters using the CASTEP plane-wave DFT code [17]. The Perdew–Burke–Ernzerhof (PBE) [21] as our was adoted as the exchange-correlation functional. A 4x4x4 Monkhorst pack k-mesh sampling was used to sample the Brillouin zone and ultrasoft pseudopotentials (US) [22, 23] where used as implemented in the CASTEP code. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) [24] algorithm with a force and stress convergence tolerance of 0.05 eV/Å and 0.1 GPa was used to ensure successful optimisation with the CASTEP code. The ONETEP calculations were performed using the projector augmented wave (PAW) method [25], within the ensemble-DFT (EDFT) method [26], which allows large-scale DFT calculations on metallic systems. the psinc basis set kinetic energy cutoff was set to 800 eV all NGWFs of 8.0 a0 radii for geometry optimisations calculations. The calculations in this work were carried out with both the ferromagnetic (FM) and antiferromagnetic (AFM) spin polarization of the spin on the Mn ions. The CASTEP code was used to benchmark as a reference code to validate our calculations with the ONETEP linear scaling code [15] for intercalation potential calculations.

2.3. Average Intercalation Potentials

Lithiation of the $Li_xMn_2O_4$ electrode materials was carried out per conductive ion occupancy description of the spinel i.e. with two distinct plateaus between $0 < x < 1$ and $1 < x < 2$ in the voltage profiles. Topotactic delithiation and lithiation of $Li_xMn_2O_4$ is considered for calculation of average Li intercalation potentials. For $0 < x < 1$, Li atoms occupy 8a tetrahedral sites whilst the second discharge plateau occurs with all Li atoms occupying 16c octahedral sites [8]. This average intercalation potential when lithiating a material Li_xX from $x = x_1$ to x_2 i.e. Li into $Li_xMn_2O_4$ vs Li/Li^+ is calculated using DFT [27, 28] and given by:

$$\langle V \rangle = \frac{-[E(\mathrm{Li}_{x_2}X) - E(\mathrm{Li}_{x_1}X) - (x_2 - x_1)E(\mathrm{Li})]}{(x_2 - x_1)e},$$

where E is the total energy as calculated using DFT, and e is the absolute value of the electron charge.

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3. Results

3.1. Structural Properties

Here we demonstrate results of structural relaxation for spin-polarised $Li_xMn_2O_4$ structures, during which, volume and internal coordinates were relaxed to minimize the lowest energy. The lattice parameters obtained after the structural relaxation of delithiated (Mn_2O_4) and lithiated spinel ($LiMn_2O_4$) are depicted in figure 3. The lattice parameters for the delithiated spinel system are not affected much by the spin ordering as all Mn are in the 4+ charge state. They are within 1.12% agreement with experimental values which is a slightly better comparison as opposed to1.74% error between the VASP [10] value and experimental value for Mn_2O_4 parameters.

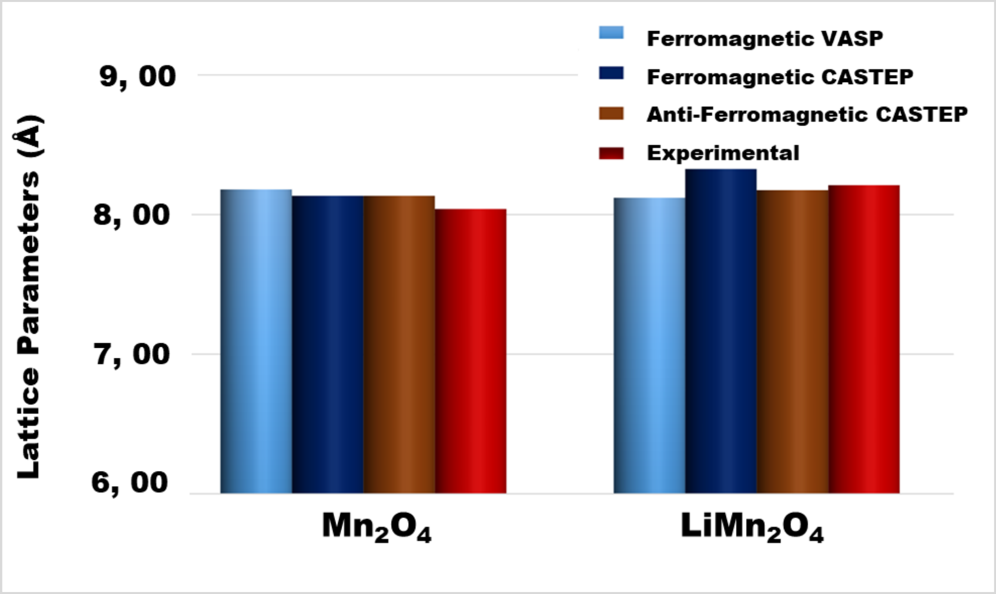

Figure 3: Lattice parameters of delithiated (Mn_2O_4) and lithiated ($LiMn_2O_4$) spinel cathode material after spin-polarized geometry optimisation of ferromagnetic (navy blue) and antifferomagnetic spin ordering (brown) simulations. The values are compared with values from literature, obtained using ferromagnettic spin ordering [10] and experimental values of 8.04 and 8.21 □, for Mn_2O_4 and $LiMn_2O_4$, respectively [ref].

Figure 4 demonstrates the relative volume errors of computatational values obtained after structural optimisation of atomic positions and lattice parameters. The computational volume values in this study are 67.27 and 68.28 for Mn_2O_4 and $LiMn_2O_4$, respectively. The literature

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volume values obtained in other computational studies using GGA+U-PAW (70.74 and 73.88 Å ^{3}) [8], HSE06-PAW (65.81 Å ^{3} for Mn_2O_4 and 70.25 Å ^{3} for $LiMn_2O_4$) [28], are compared with with experimental values of 66.36 Å ^{3} for Mn_2O_4 and 69.89 Å ^{3} for $LiMn_2O_4$ (red) [28]. The volumes for the delithiated Mn_2O_4 are overestimated by 1.37% by GGA-Ultrasoft pseudopotentials in our work, 0.86 % GGA-PAW and 6.60 % by GGA+U-PAW. On the other hand, lithiated GGA-US underestimates volume for spinel $LiMn_2O_4$ by 2.27 %, close to the underestimation by GGA-PAW, while GGA+U-PAW greatly overestimates the volume [8]. The hybrid functional HSE06-PAW yields the smallest overestimation of 0.52 %.

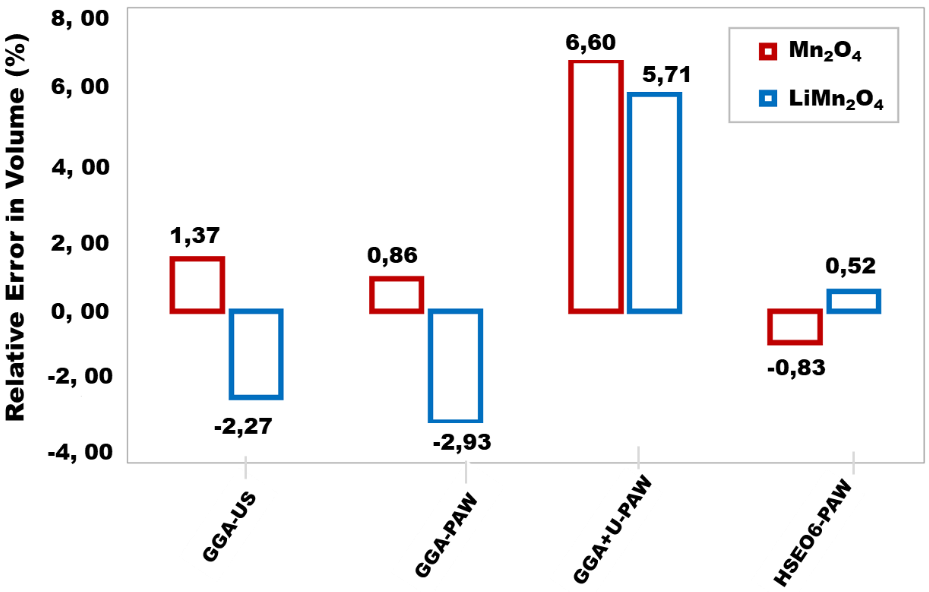

Figure 4: Relative volume error for the topotactic delithiated (red) and lithiated (red) phases when using GGA-ultrasoft (this work), GGA-PAW (light blue) [10], GGA+U-PAW [8] and HSE06-PAW [28] compared to experimental values.

3.2. Average Intercalation Potentials

Total energy optimisation in the ONETEP code was carried out using PAW pseudopotentials for the purpose of benchmarking the reliability of the code in comparison to the conventional plane-wave approaches (CASTEP). Total energy optimisation in the ONETEP code was carried out using PAW pseudopotentials in order to produce results comparable to conventional plane-wave calculations (in CASTEP) using ultrasoft pseudopotentials. The average intercalation potentials depicted in figure 6 were calculated using equation (1). The average

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intercalation potentials depicted in figure 5 were calculated using equation (1). The CASTEP (blue sphere) and ONETEP (green sphere) values for the first cycle demonstrate relatively comparable results (3.20 and 3.39 V, respectively) to each other and to the voltage value obtained from literature using VASP code (3.37 V).

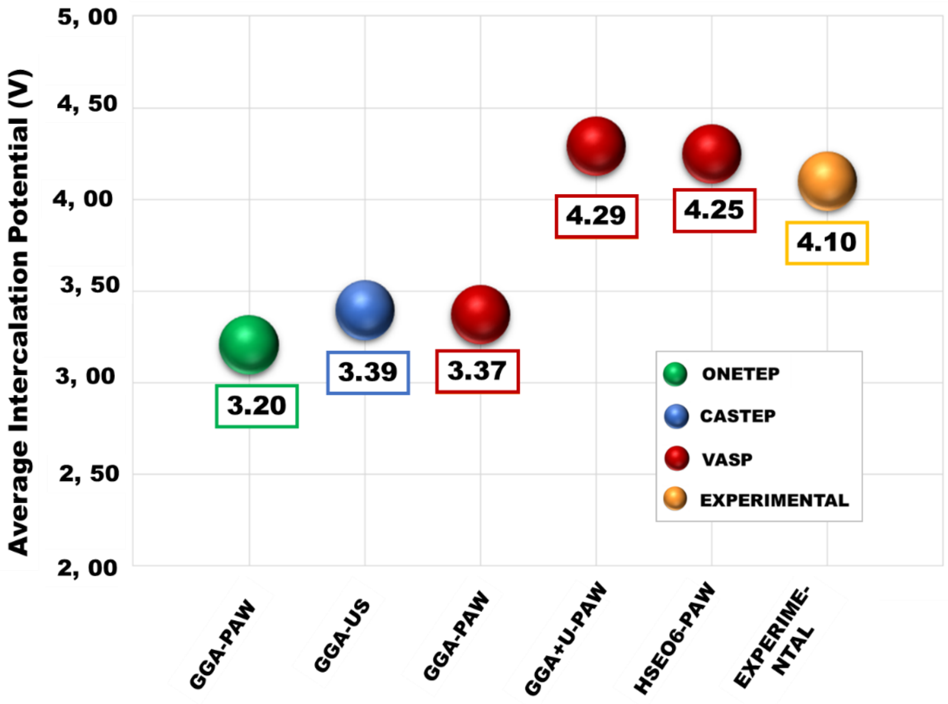

Figure 5: Average Li intercalation potentials vs. Li/Li+ in volts, obtained using ONETEP (green), CASTEP (blue) converged with 800 eV kinetic energy cutoff. Literature VASP values (red) [8, 10, 28] and experimental value (orange) [8].

Fig 6 shows the relative intercalation potential errors in relation to experimental values obtained using functionals from various simulation codes i.e. ONETEP (green), CASTEP (blue) and VASP (red). The values from GGA suggest ~0.7 V intercalation potential on average, with approximately 20 % error. On the other hand, GGA+U yields values close to experiment although it slightly overestimates the intercalation potentials by a factor of 0.1 V under 5%. Moreover, HSE06 yields potentials that agree better with experimental values than those calculated with GGA.

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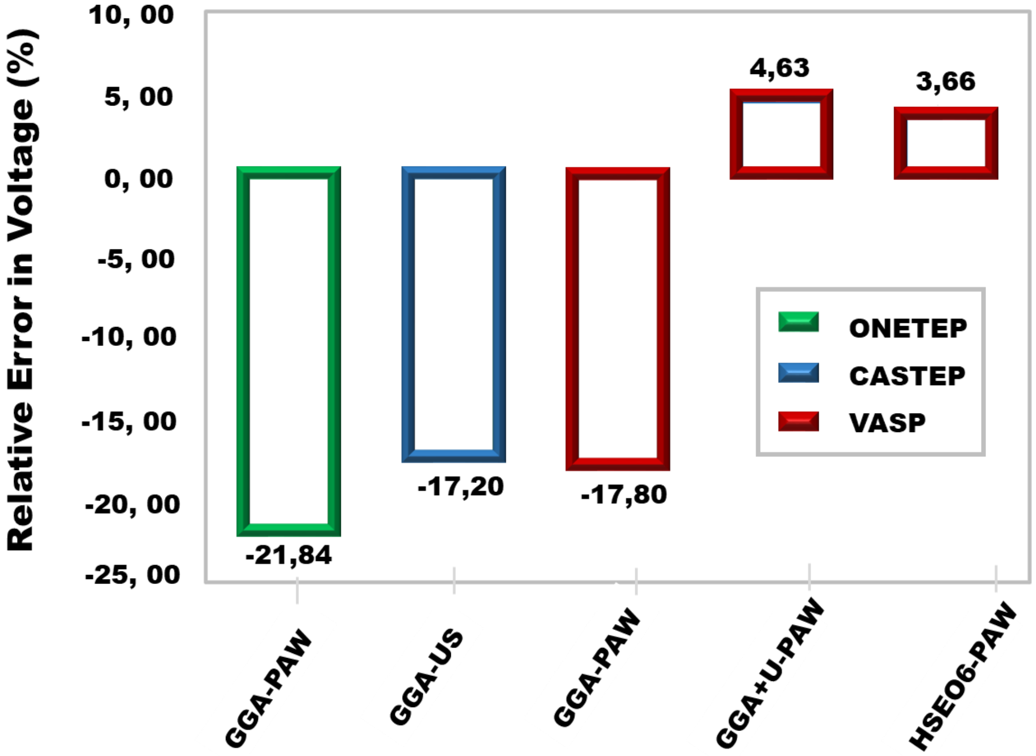

Figure 6: Relative percentage error obtained from comparing experimental intercalation potentials to those obtained computationally using ONETEP (green)-this work, CASTEP (blue)-this work and VASP (red)-literature [8, 10, 28].

4. Discussion

A series of antiferromagnetic (AFM) and ferromagnetic (FM) spin ordered GGA calculations for topologically delithiated and lithiated spinel manganese oxides were presented. The level of exchange-correlation correction, as well as the spin order, are found to be essential for reproducing the correct structural ground-state composition of $Li_xMn_2O_4$ [1]. The structural properties of all spinel systems were found to be consistent in line with values from the literature for both lattice and volumetric values. The intercalation voltages for GGA with various codes i.e. CASTEP, ONETEP and VASP show good agreement small absolute relative error with each other as they yield but not with experimental values.

As such, it may be crucial to consider opting for either HSE06 and GGA+U. It has been reported that only GGA+U and HSE06 successfully result in evident charge disproportionation hence the presence of Jahn-Teller distortions, for electrode materials such as $LiMn_2O_4$ [8, 28].

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In the study of redox reactions involving localized electrons, the former may drastically improve the intercalation potentials given attainment of appropriate U-parameters for the spinel metallic states. As it stands, HSE06 functionals are more cost-intensive than for GGA or GGA+U [28], hence GGA+U may be considered for modelling electrochemical performance for larger electrode systems [16].

Nonetheless, it stands that the GGA calculations obtained using the conventional DFT code (CASTEP) result in intercalation values that are consistent with previous findings indicating the typical GGA under binding [28] trend. The retention comparable voltage values using GGA functional in various codes, with that obtained using the ONETEP code, with a difference only a deviation of 0.19 V, promises possible improvement of future GGA+U as obtained using GGA+U in previous study [8]. These findings open room for exploring the DFT+U capabilities of the both CASTEP and ONETEP codes [29], in future work, to improve the intercalation voltage value.

5. Conclusion

In the current study, the intercalation potential for spinel redox in $Mn_2O_4/LiMn_2O_4$ was computationally modelled by carrying out structurally optimization calculations for delithiated and lithiated spinels using different DFT codes. Structural properties (volume and lattice parameters) of ground state models yielded values within 3 % error of experimental results for GGA calculations. Furthermore, this study has demonstrated the relative accuracy of the linear-scaling DFT method when compared with traditional cubic scaling DFT approaches with intercalation potential values within 3% error with each other. These findings add significant value to developments of accurate electronic level calculations for much larger systems. As such, it is greatly anticipated that linear scaling DFT will enable the study of larger and more models of candidate electrode materials for future voltage predictions and consequently capacitate the discovery of new materials with potential to be considered as future cathodes, pending exploration of other functionals that improve on the underestimation of GGA such as the DFT+U component in both CASTEP and ONETEP codes. The findings of this study demonstrate that viability to perform reliable and coherent linear-scaling DFT calculations for metallic systems. It is further envisaged that the approach will be employed in calculations of voltage profiles for larger lithium ion battery electrodes nano-architectures (nanoparticles,

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nanorods, nanosheets and nanoporous structures) consisting of more that 3000 atoms, which have been generated spontaneously by simulated amorphisation recrystallization methods, where classical forcefields were invoked [16].

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Declaration of Interest Statement

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☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Ngoepe PE, Ledwaba RS, Womack J and Skylaris C.-K. :Conceptualization

Ledwaba RS: Data curation

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Ledwaba RS and Womack J: Investigation

Ledwaba RS, Womack J and Skylaris C.-K.: Methodology

Ledwaba RS:Project administration

Ngoepe PE: Resources

Ngoepe PE: Software

Ngoepe PE, Womack J and Skylaris C.-K. Supervision

Ngoepe PE, Ledwaba RS, Womack J and Skylaris C.-K. Validation

Ledwaba RS: Visualization

Ledwaba RS: Roles/Writing - original draft;

Ngoepe PE, Ledwaba RS, Womack J and Skylaris C.-K. : Writing - review & editing