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# Ab Initio Molecular Dynamic Simulation of the Ionic Transport Mechanisms for LiCoO2 and Ni Doped LiCoO2 as Cathodes in Lithium Batteries

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*Abstract*— **Ab initio molecular dynamic simulation of $LiCoO_2$ and Ni-doped $LiCoO_2$ is studied to determine the ionic transport properties of both materials relying on their electronic structure information. Results obtained from the study suggest doping $LiCoO_2$ with Nickel affects the energy band gap of $LiCoO_2$ making the energy band gap narrower thereby enhancing the electronic conductivity of the material. Also, from the Ab initio MD simulation results of $LiCoO_2$ and nickel-doped $LiCoO_2$. Ni-doped $LiCoO_2$ is a better ionic conductor with a higher lithium ion diffusion rate than $LiCoO_2$ cathode material at a temperature of 300 K (at high temperature). Indicating the ionic transport mechanism of undoped $LiCoO_2$ cathode material is improved when doped with Nickel.**

***Keywords—Electronic structure; Transport mechanism; Activation energy; Self Diffusion Coefficient; Density Functional Theory***

## I. INTRODUCTION

In addition to electronic structure methods employed in the study of condensed matter systems and solid-state cathode materials, are the interatomic potential-based methods which includes Molecular Dynamics (MD) techniques. MD simulation is a technique to simulate the motion of atoms and molecules under predefined conditions such as temperature, pressure, stress, external forces and many more. MD simulations can therefore be used to study dynamical processes at the nanoscale and to calculate a broad range of properties, for example, phase diagrams, diffusion coefficients, ionic conductivity and various response functions, as well as static quantities such as radial distribution functions, coordination numbers, elastic moduli and more [1] [2]. The molecular dynamics technique consists of numerically solving Newton's equations of motion for a large ensemble of particles at a finite temperature and pressure. Repetition of the integration algorithm over many time steps yields a detailed picture of the evolution of ion positions and velocities as a function of time. Within the current context of condensed matter (solid state) and Li-ion conducting materials properties, MD simulations are good at providing diffusion coefficients, stress, pressure, elastic limit and ionic transport mechanisms as functions of temperature [3] [4][5][1]. A widely used MD code is the DL_POLY program and ab initio MD. It is worth noting that potentials-based MD simulations on Li diffusion can now regularly be run for timescales on the order of nanoseconds, at least two orders of magnitude longer than ab initio MD calculations of much smaller systems [6]. Indeed, the advantage of interatomic potential-based methods is that they are computationally inexpensive and thus allow large ensembles of atoms, from thousands to millions, to be handled efficiently within a reasonable time frame on modern supercomputers. The chief disadvantage is that explicit information on the material's electronic structure obtained from the use of electronic structure methods is not included in most potential-based methods [7]. Hence, the use of ab initio MD simulations which rely on information from electronic structure methods. Computational tools will therefore be critically important to enable real-world materials development, optimization or minimization of traditional experimental testing, and prediction of materials performance under diverse conditions [8].In this research, ab initio MD simulation is used to study the ionic transport properties of $LiCoO_2$ and Ni doped $LiCoO_2$ as cathodes in lithium batteries.

## II. THEORY

For the system of particles interacting pairwise by Lennard Jones forces derived from Lennard Jones Potential, Classical equations of motion can be used to describe the motion of the system of interacting particles. Using the Classical Approach, the calculation of thermodynamic averages in an equilibrium system is taken along the particles trajectory/path at different times. Also, the speed or velocity of the system of interacting particles is modeled with the Maxwell-Boltzmann velocity distribution function, $f(v)$ given by

$$f(v) = 4\pi v^2 (\frac{m}{2\pi KT})^{\frac{3}{2}} e^{\frac{-mv^2}{2KT}} \quad (1)$$

let$E_k = \frac{1}{2}mv^2$, the translational kinetic energy $E_k$ then equation (1) can be written in terms of the energy as

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$$f(E_k) = \frac{8\pi}{m}(\frac{m}{2\pi KT})^{\frac{3}{2}}\epsilon e^{-\frac{\epsilon}{KT}} \qquad (2)$$

The curve obtained from this function has a peak at $E_k = kT$, then $e^{-\left(\frac{Ek}{kT}\right)} = \frac{1}{e}$ for which $f(E)$ is maximum at the maximum velocity of the system of interacting particles. At zero temperature, the kinetic energy and velocity is zero whilst at very high temperature values the kinetic energy and velocity turn to decrease approaching zero. Also $f(E)$ is temperature dependent and assuming thermal equilibrium conditions occur at the most stable position which is at the peak then the average kinetic energy is

$$E_k = \frac{3}{2}NKT \qquad (3)$$

for N number of particles in the interacting system taken into account the assumptions of the Kinetic – molecular model. This implies that if the kinetic energy that relates to the velocity of the interacting particles can be determined at every temperature then the Maxwell Boltzmann velocity distribution function (equation (1)) can be used to monitor the velocity.

Let us consider the velocity auto-correlation function C(t) which decays with time due to collisions of the interacting particles in the system that is given as

$$C(t) =< v(t)v(to) > \qquad (4)$$

An integration of equation (4) gives the mean squared path displacement of the interacting particles over time given as

$$\Delta x^2 =< (x(t) - x(to))^2 > \qquad (5)$$

Brownian motion can be used to model the motion of the interacting particles in the system this can be ballistic or diffusive motion depending on the path of the interacting particles. Now that we know the velocity distribution function of the interacting particles. We seek to find the path followed by these particles over time. Using Brownian motion, the motion of the interacting particles are considered to have a fluctuating force, $F(t)$ and a damping constant (gamma) govern by an equation of motion similar to that of damped oscillations and given as

$$\dot{v} + \gamma v = F(t) \qquad (6)$$

which is a first or second order differential equation depending on the form of the fluctuating force with solution that give rise to a velocity auto-correlation function of the form as in equation (7)

$$C(t) =< v(t)v(to) >= \frac{kT}{m}e^{-\gamma(t-to)} \qquad (7)$$

Since the velocity is seen to decay exponentially. This implies we can now determine the squared displacement at any given time by integrating equation (7) that is the velocity auto-correlation with respect to time for a given time interval. Let us consider integrating equation (7) over the time interval $[t_o, \infty]$, that is from the initial time through to infinity. Then we have

$$\begin{aligned}\int_{t_o}^{\infty} c(t)\,dt &= \frac{kT}{m}\int_{t_o}^{\infty} e^{-\gamma(t-t_o)}dt \\ &= \frac{kT}{m\gamma}\left[e^{-\gamma(0)} - e^{-\gamma(\infty)}\right] = \frac{kT}{m\gamma} \\ &= x(t_o)^2\end{aligned}$$

, this is the squared displacement at time $t_o$.

Again, let's consider integrating equation (7) over the time interval $[t_o, t]$, that is from the initial time through to a much later time. Then we have

$$\int_{t_o}^{t} c(t)dt = \frac{kT}{m\gamma}\left[1 - e^{-\gamma(t-t_o)}\right] = x(t)^2$$

From the results obtained from the two integrations we can determine the mean squared displacement $\Delta x(t)^2 =< (x(t) - x(to))^2 >$ as

$$\Delta x(t)^2 = \frac{2kT}{m\gamma}(t - t_o) - \frac{2kT}{m\gamma^2}\left(1 - e^{-\gamma(t-t_o)}\right) \qquad (8)$$

The first term of equation (8) represents the Diffusive motion of the particle over large time difference. Hence the first order approximation gives us a mean squared displacement that is

$$\Delta x(t)^2 = \frac{2kT}{m\gamma}(t - t_o) \qquad (9)$$

If we let $D = \frac{kT}{m\gamma}$ referred to as the diffusion constant given by Einstein relation, we have equation (9) reduced to

$$\Delta x(t)^2 = 2D(t - t_o) \qquad (10)$$

In 3 dimensional coordinates, equation (10) is represented as

$$2D(t - t_o) = \frac{1}{3}\Delta x(t)^2 \tag{11}$$

A graph of the mean squared displacement verse time when extrapolated/fitted to a linear curve has slope equal to 6 times the Diffusion constant, D. [9] [10] [11]

The ionic conductivity is related to the diffusion coefficient using the Nernst-Einstein equation as

$$\sigma = \frac{(\rho z^2 F^2)D}{RT} \tag{12}$$

Representing the Diffusion coefficient in Arrhenius form as in equation (13) and inserting into equation (12).

$$D = D_o exp\left(\frac{-E_a}{KT}\right) \tag{13}$$

we have

$$\sigma = \frac{\left[(\rho z^2 F^2) D_o exp\left(\frac{-E_a}{KT}\right)\right]}{RT} \tag{14}$$

let $A = \frac{\rho Z^2 F^2}{R}$ then equation (14) reduces to

by

$$\sigma = \frac{\left[A D_o exp\left(\frac{-E_a}{KT}\right)\right]}{T} \tag{16}$$

working out the algebra and making the activation energy, $E_a$ the subject of equation (16) we have

$$E_a = -KTIn\left(\frac{\sigma T}{A * D_o}\right) \tag{17}$$

where the symbols /rho is the molar density of diffusing alkali metal ions in the unit cell, z is the charge number on alkali metal ions, F is the Faraday constant, R is the gas constant, $D_o$ is the constant at infinity, $E_a$ is the activation energy for diffusion and K is the Boltzmann constant. All other symbols in the equations have their usual meaning [12].

## III. METHODS

The electronic structure methods for obtaining the total ground state/ minimum energy is achieved using the First-principles calculation with Spin Polarized Density Functional theory as implemented on the Quantum Espresso Software Package . Pseudopotential is Ultrasoft + core correction with augmented plane wave energy and charge density cut off at 25 Ry and 500 Ry respectively. The exchange correlation functional is described by Perdew-Burke-Ernzerhof (PBE) within the Generalized Gradient Approximation (GGA) with an electron beta mixing of 0.4. Convergence with respect to self-consistent iterations followed by non-self-consistent iterations is assumed when the total-energy difference between cycles is less than $10^{-6}$ eV/atom. For the geometric optimization of the crystal structure, the Brillouin zone (BZ) was sampled using the k-point sampling method of Monkhorst-pack. Optimization of K-point grid densities over the BZ is achieved with Monkhorst- Pack by setting the electronic structure (super cell) to 5x5x1 for all Electronic Structure Calculations for the total minimum energy, Fermi Energy level, Energy bandgap and density of state. Next, Nickel doping of LiCoO2 is implemented and used in the computational study of the electronic properties following the approach employed in the study of the electronic properties of $LiCoO_2$.

### A. *Ab initio M*D Simulation method

Ab initio Molecular Dynamic Simulation depended on the electronic structure methods to help implement the NVT ensemble at constant energy for some number of iterations at a setting for ionic motion dynamics within a time step of 0.5 femto seconds at different temperatures. At the end of the ab initio MD simulations run the output obtained from the simulation provides information on the mean squared displacement at an instant in time and the average diffusion coefficient of the individual atoms in the material under study. This ab initio MD simulation method is employed for $LiCoO_2$ and Ni doped $LiCoO_2$ studies. Data obtained from the output file is used to plot a graph of the mean squared displacement as against the time while the diffusion coefficient is obtained by linear fitting/extrapolation of the graph. With the information from theory, the conductivity is plotted as a function of inverse temperature and the activation energy plotted as function of temperature [10] [11].

## IV. RESULTS AND DISCUSSIONS

The Fermi energy level represented by the vertical line, colored green and centered on the energy value of 12.137 eV on the energy axis, falls in a dip as shown on the Density of States (DOS) plot on Fig 1 with the red legend representing DOS curve. This means the material is either a semiconductor or an insulator. However, knowledge of the value of band gap which is 1.4161 eV indicates the material under study is highly predicted as a semiconductor since the energy gap is less than 3.0 eV as was obtained from the calculation of the energy band gap. Due to the small energy band gap, at room temperature, some electrons from the

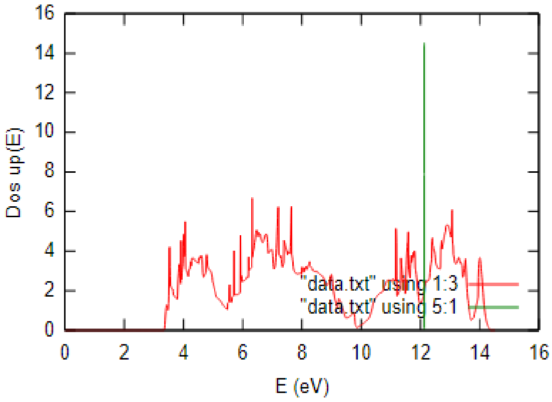


**Fig. 1.** Density Of States plot for $LiCoO_2$

valence band can acquire enough energy to cross the energy band gap and enter the conduction band. However, if the material is a semiconductor, is temperature dependent and an increase in temperature would reduce the energy band gap further making it easy to conduct electricity.

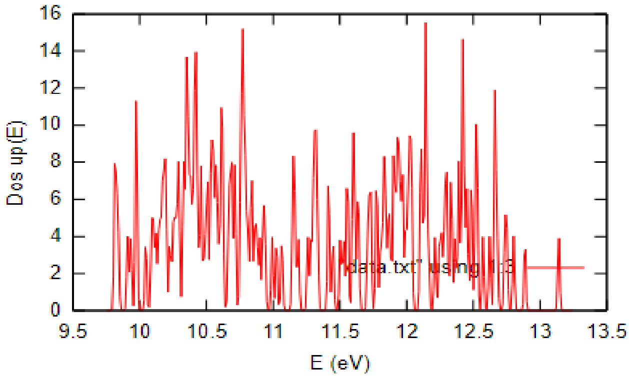


Fig. 2. Density of States plot for Ni doped $LiCoO_2$

Fig. 2, displays the density of states plot for Ni doped LiCoO2. The fermi energy surface line when drawn would be centered at the energy value of 11.442 eV on the energy axis. This fermi energy surface line would fall in a dip indicating Ni doped LiCoO2 is a semiconductor material which is expected to have a much narrower or smaller band gap than that of LiCoO2 since it is doped with Nickel (Ni) which is metallic. Hence the Ni doped LiCoO2 material can conduct electricity more than LiCoO2 material whenever temperature increases since more valence electrons in the valence band can easily cross a much narrower band gap into the Conduction band.

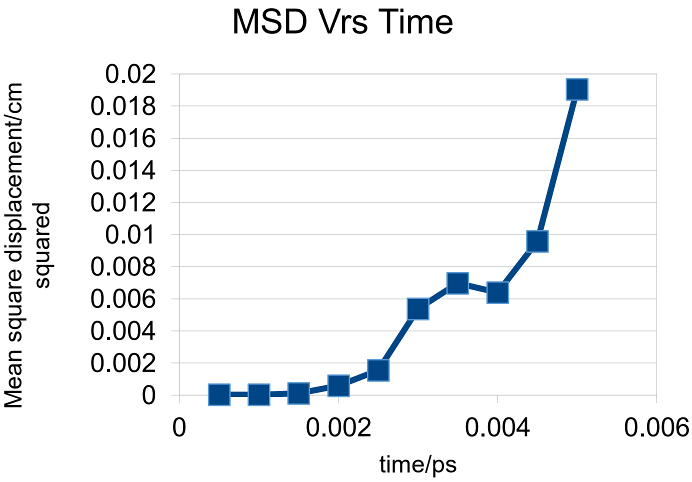


**Fig. 3.** A graph of Mean Squared path Displacement verse time (LiCoO2)

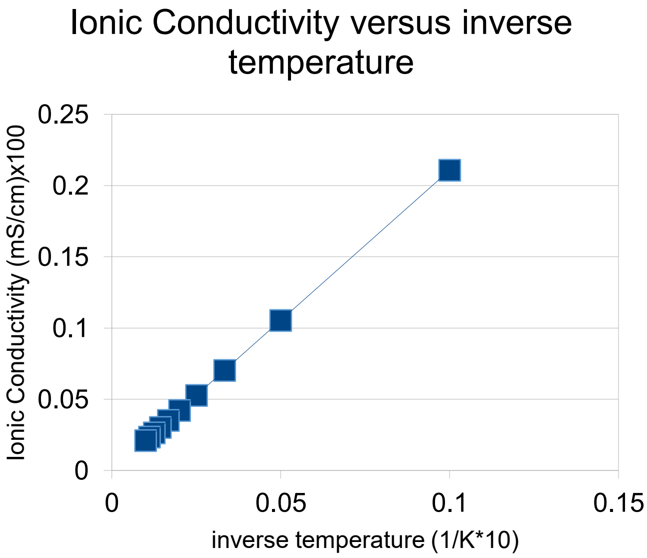


**Fig. 4.** Displays a graph of the conductivity as against the inverse temperature (LiCoO2).

The self-diffusion/ Diffusion coefficient of Lithium ion for both $LiCoO_2$ and Ni doped $LiCoO_2$ material was determined to be 0.0002107 cm squared/s and 0.0003303 cm squared/s by Linear extrapolation of the graph of mean squared path displacement with respect to time on fig. 3 and fig. 6 respectively. The results obtained for the diffusion coefficient of Lithium ion in $LiCoO_2$ and Ni doped $LiCoO_2$ by linear extrapolation of fig. 3 and fig. 6 was approximately same to that obtained from the ab initio MD simulation of both materials, where the combined diffusion of the center of mass of the atoms in a given material is determined as the Diffusion coefficient for either $LiCoO_2$ or Ni doped $LiCoO_2$ material under study. The Diffusion Coefficient obtained from the ab initio MD simulation is 0.0001702 and 0.00032885 for $LiCoO_2$ and Ni doped $LiCoO_2$ material respectively.

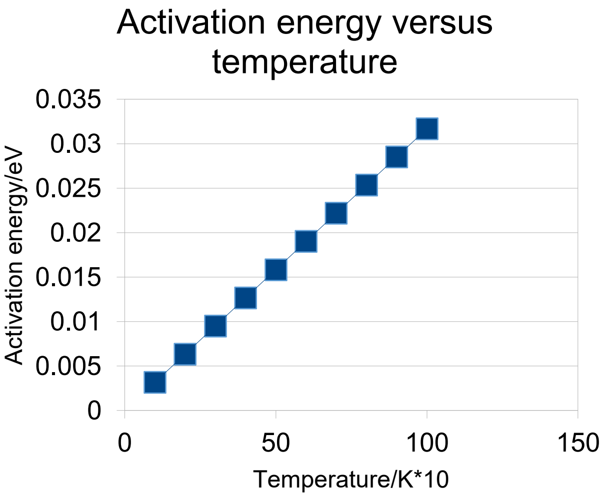


Fig. 5. A graph of Activation verse the temperature (LiCoO2).

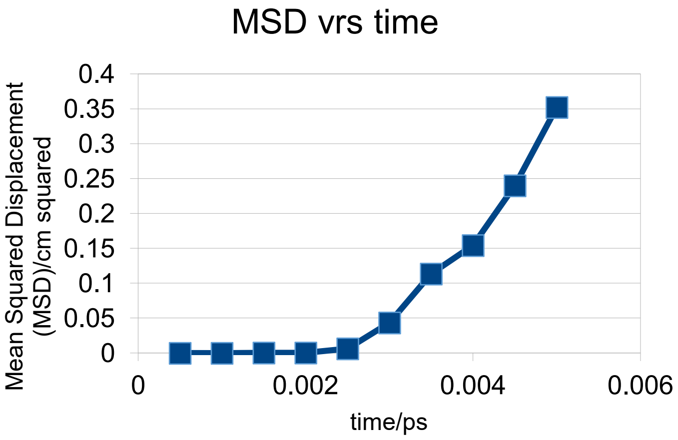
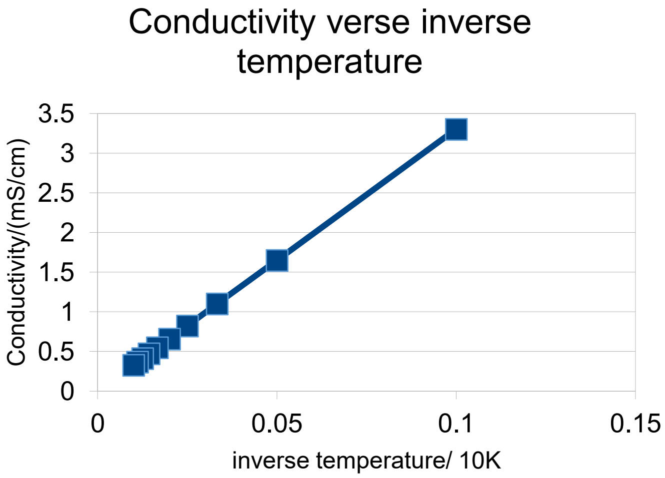


**Fig. 6.** A graph of Mean Squared path Displacement verse time (Ni doped LiCoO2)

For both LiCoO2 and Ni doped LiCoO2 material, the ionic conductivity and activation energy is observed to be temperature dependent on fig. 4, 5, 7 and 8. Clearly, an increase in temperature decreases the ionic conductivity whilst the activation energy increases as seen on fig. 4 & 7 and on fig. 5 & 8 respectively. Hence on these figures at a temperature of 300 K, the ionic conductivity is found to be 7 mS/cm for LiCoO2 and 11 mS/cm for Ni doped LiCoO2 whilst the activation energy/barrier is found to be 0.095 eV for LiCoO2 and 0.0899 eV for Ni doped LiCoO2 as tabulated on table 1.

**Fig. 7.** A graph of Conductivity verse inverse temperature (Ni doped LiCoO2)



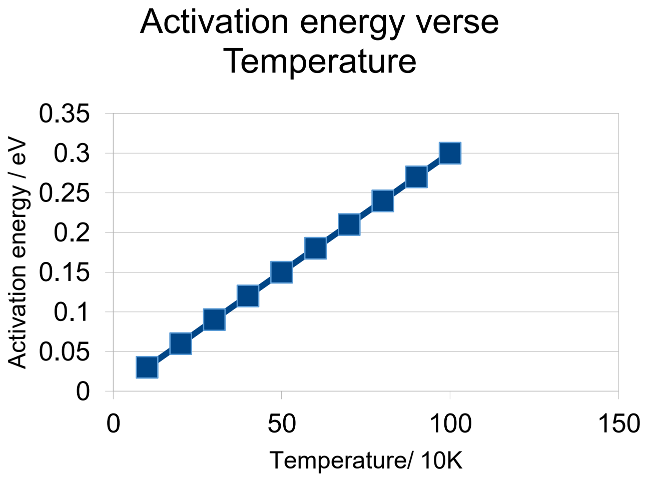


**Fig. 8.** A graph of Activation energy verse temperature (Ni doped LiCoO2)

**Tab. 1**: Displays the results obtained from the graphs plotted for the Activation energy, Ionic conductivity and Diffusion Coefficient at 300 K.

| | Activation energy /eV at 300 K | Ionic Conductivity/ mS/cm at 300 K | Diffusion Coefficient / cm squared/s |
|---|---|---|---|
| LiCoO2 | 0.0950 | 7 | 0.0002107 |
| Ni doped LiCoO2 | 0.0899 | 11 | 0.0003303 |

From the tabulated results, the Diffusion Coefficient and the Ionic conductivity of $LiCoO_2$ material is increased when $LiCoO_2$ material is doped with Nickel (Ni) whilst the activation energy slightly decreases at a temperature of 300 K. This means Ni doped $LiCoO_2$ material when used as a cathode material in batteries would be a better ionic conductor with enhanced ionic transport properties than undoped $LiCoO_2$ material.

## V. CONCLUSION

Thorough analysis of the results obtained suggest Doping $LiCoO_2$ with Nickel would have an effect on the energy band gap of $LiCoO_2$ making the energy band gap narrower thereby enhancing the electronic conductivity of Ni doped $LiCoO_2$ since more electrons in the valence band can easily cross the narrower energy band gap into the conduction band to aid in the conduction of electricity. Also, from the Ab initio MD simulation graphs of $LiCoO_2$ and Nickel doped $LiCoO_2$ material. The ionic conductivity and activation energy depends on temperature with an increase in temperature decreasing the ionic conductivity while the activation energy increases. However, from the tabulated results Ni doped $LiCoO_2$ is a better ionic conductor with higher lithium ion diffusion rate (Diffusion coefficient) than $LiCoO_2$ cathode material at a given temperature of 300 K.

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