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ON THE VIGOR OF NEB METHODOLOGY TO EXPLORE DIFFUSION MECHANISM IN LITHIUM-ION BATTERIES

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Abstract

The electrical energy required by modern devices including portable electronics and electric vehicles is usually provided by lithium-ion batteries (LIB) which have earned prime research and industrial attention these days. The issues which are being addressed to improve the performance of LIBs include charge/discharge rates, power/energy density, reliability and cost. The charging and discharging processes involve diffusion of lithium ions which is key transport mechanism in the LIB. The understanding of diffusion and related parameters is at heart of LIB which is achieved by different experimental methods and theoretical strategies which works to provide an access to minimum energy path (MEP) of the ions. The current computational resources are very helpful to find MEP via number of techniques out of which nudged elastic band (NEB) is very easy and effective molecular dynamics-based method. This review sheds light on diffusion mechanism involved in LIBs and a comprehensive look into NEB study of the ionic transport to find the MEP for transition states. The diffusion processes related to lithium ions in different reported materials using NEB method for finding minimum energy barrier of hooping are described.

1. Introduction:

Energy is one of the main issues of the world due to increased usage of electrically driven appliances. The available energy sources are not sufficient to cope with the requirements of electronic devices including household portable devices, energy storage and electric vehicles. The world is no more relying on conventional energy sources like gas, oil, coal, wind, thermal and nuclear energy sources due to their depletion and environmental hazards that has turned the attention towards alternate renewable energy sources. Considering these issues, the rechargeable lithium-ion batteries (LIBs) emerged as reliable option to store energy due to its better performance in terms of cyclability, stability, user friendly atmosphere and cost. Further, the research is in progress to solve the issues to improve the performance of batteries like weight, stability, power density, energy density, life span etc [1].

The current era is the period of energy sources and devices since our planet is being depleted of the energy sources due to which researchers are facing

severe challenge to meet up the energy demands with a reliable, affordable and modern substitute. The alternate sources should be environment friendly as the conventional sources of renewable energy are drastic to human health [2-5]. The technologists and researchers from all over the world are giving their best to find solutions to meet with the future demands of energy. The 2030 agenda for UN general assembly known as transforming our world is also based on developing the sustainable energy devices [6]. Sun is known as the champion of energy; this is believed that earth receives 174 petawatt of energy yearly [7]. And our planet absorbs 3850 zeta joule of this total [8, 9]. This plenty of energy in hour is much more then what we use in one year, so if we are able to harvest it properly the problem of energy will be nothing for us, we can also understand the magnitude of this enormous amount of energy with the considering that amount of energy that we obtain from sun in one year will be the double of the amount that we will ever be able to harvest from all renewable energy sources of coal, gas, water and wind [10]. In what follows, a brief description of the renewable energy devices is given.

1.1 Super capacitors:

Supercapacitors are similar to traditional capacitors with high capacitance in which energy is stored by static charges instead of electrochemical reaction as it happens in batteries [11]. These are also known as ultra-capacitors (UCs) or Electric double layers capacitors (EDLCs) These are categorized with respect to electrodes; EDLCs, Pseudo Capacitors and Hybrid Capacitors are the major types of super capacitors. EDLCs Electrochemical Double Layer supercapacitor is cheaper technology among these, It consist of double layer of carbon electrodes along with separator dipped in electrolyte, pseudo capacitor use metal oxide instead of copper electrode Supercapacitor have high storage capabilities, greater power density and good cycles life but problem here is their cost, which is about 20000 $/kWh. Researchers are trying to reduce the cost by modifying electrodes, electrolyte and separator in the capacitors [12].

1.2 Fuel cells:

A chemical device that changes chemical energy into electrical power basically by electrolysis known as fuel cell. Major advantage of fuel cells is its production of water and heat as byproduct instead of CO_2 so it is a major element to reduce the pollution There are different types of fuel cells are considered; Direct methanol fuel cells, proton exchange membrane fuel cell, phosphoric acid fuel cells, alkaline electrolyte fuel cells, molten carbonate fuel cells and solid oxide fuel cells [1, 13-15].

1.3 Batteries:

An electrochemical device which changes chemical energy directly into electrical energy known as battery. The batteries are the major candidates of today energy fields, and they are widely being applied in electronics and even in power machines as well. These are also the highly recommended solution for modern pollution free transport. The current communication and transport technologies are relying strongly on rechargeable batteries. However, the batteries are facing problems of low energy density and low power density this has attracted the researchers from all over the world to propose reliable solution for these. [16, 17]. Major challenges to batteries are low energy density, power density, high cost and its safety.

Although all parts of battery are important to determine the quality parameters of a battery, but electrode and electrolyte are highly concerned where all the chemical reactions occur. Especially the cathode material is the major element in determining the prescribed qualities of a battery and so it also determine the cost of a battery. Cathode is the intercalation material and it start the charge and discharge process by oxidation and reduction of metal cation and Li atom during discharge and charge process respectively. Gravimetric density of a battery is determined by the stored material inside the cathode. While power density is determined by the movement of Li^+ ions inside the material, [17]. Low energy density is due to availability of relatively less intercalation sites at anode material [18]. Post-LIBs use mechanism of "beyond intercalation" ion storage, those have higher energy densities but are unstable and have less cycles and due to instability and phase

transition of active materials reason for that is uncontrolled reactions at electrolyte and electrodes [19]. Improvements are needed at electrodes and electrolyte material for realization.

There are three major types of batteries that are mainly used today which are lead acid batteries, nickel-based batteries and lithium-based batteries. In this lead-acid battery is the ancient category of rechargeable batteries in which lead dioxide acts as cathode, lead as anode and Sulphuric Acid behaves as electrolyte. Rated voltage for lead acid batteries is 2 V, energy density 30 Wh/kg and power density about 180 W/kg along with energy density about 85% to 90% [20]. These can be easily installed, no need of maintenance and are relatively cheaper. The idealism for long term storage in this battery is its self-discharge rate at 25 ℃ is about 2%. These batteries face the drawback of their poor operational lifetime, low cycle life, deep discharge affect and small temperature range (Temperature should never exceed about 45℃, higher temperature can affect capacity as well as reduce battery life and efficiency). Life span of lead acid batteries is 1200-1800 charge, discharge cycles, or 5 to 15 operating years.

In nickel based batteries there are mainly: nickel cadmium (NiCd), nickel metal hydride (NiMH) and nickel zinc (NiZn) batteries [11]. Entirely the three categories of nickel-based batteries use same positive electrode which is nickel hydroxide and electrolyte potassium hydroxide with lithium hydroxide. In case of negative electrode cadmium hydroxide, metal alloy and zinc hydroxide is being used respectively. Rated voltage for these batteries is 1.2-1.65 V, energy density about 50-80 Wh/kg that is higher than lead acid batteries and life cycle of about 1500-3000 for NiCd while lower values of cycles for NiMH and NiZn than those of lead acid batteries. Generally, NiCd batteries are used for industrial applications, but it is very costly about 10 times the lead- acid batteries. These suffers with low energy efficiency (lower than lead acid batteries) and self-discharge rate is about 10% while that of lead acid batteries is 2%.

1.3.1 Lithium Batteries:

Third type is lithium-based batteries. It is typically used in cell phones and laptops. Researchers are trying to further improve their power density to use them in hybrid or electric vehicles (HEVs) and Plugged in Hybrid Electric Vehicles (PHEVs) . These are better than NiCd and lead acid batteries due to their relatively higher energy density, power density, no memory effect, nonpoisonous composing materials, less maintenance and low self-discharge rate. There are two main types of lithium-based batteries: lithium-ion batteries and lithium polymer batteries. Nominal cell voltage of lithium-ion batteries is about 3.7 V, 80-150 Wh/kg energy density and power density is about 500-2000 W/kg further self-discharge is lower not more than 5% per month and more than 1500 cycles. In the case of lithium-ion batteries over charging must be avoided to control metallic plating. [21, 22].

Almost all of the energy devices and their applications involve diffusion mechanism, that is the reason diffusion study is much important in both experimental and theoretical research work. In the coming section we will briefly discuss the solid-state diffusion that is the key feature of these devices further we will perform in depth study of Nudged Elastic Band method that is the primary method to perform the theoretical modeling of diffusion mechanism and is the most implemented method to carry out this study in all such devices.

2. Diffusion:

The diffusion of ions is the principal transport mechanism involved in charging and discharging processes of ionic batteries. The following sections are dedicated to principles, parameters and relevant details of the diffusion.

2.1 Solid state diffusion

The chemical reactions and transport of atoms along the crystal is due to solid state diffusion. Diffusion occurs due to the defects present in solids. There are several types of defects; point, line and surface defect. In point defects Frenkel defect (ions moves through interstitial sites) and Schottky defects (ions moves through vacancy) causes diffusion. In other defects linear, planar and surface defect are included which give high diffusivity than lattice diffusion. [23-26]

The irregular and random motion of small particles in any liquid was discovered very long in 17th century by Scottish scientist Robert Brown [12]. The idea of self-diffusion was given by Maxwell

while he was trying to measure the rate of gases diffusion after that diffusion was studied in condensed matter i.e. in lead metal in both solid and liquid phases.

2.1.1 Diffusion and Fick's law

For the particles moving in one-dimension, the flux of diffusing particles can be written as.

$$J = -D\frac{\partial C}{\partial x} \quad ------ (1)$$

Here J represents the flux of diffusing particles and $\frac{\partial C}{\partial x}$ represents the number density or concentration gradient. This is known as Fick's first law of Diffusion and this equation shows that flux of diffusing particles is directly proportional to concentration gradient and it decreases with the concentration. While D is here diffusion coefficient also named as diffusivity [27].

We can represent this law in three dimensions by using the vector coefficient ∇ or Dell operator. Its direction is along the maximum concentration gradient. Or we can write it as

$$J = -D\nabla C \quad ------ (2)$$

This law also has correspondence with Fourier law of heat flow and Ohm law of conduction [28].

2.1.2 Equation of continuity

This law can also be related with the equation of continuity. Equation of continuity is based on conservation of mass. We can illustrate it as, for a unit volume of liquid the total in flow and out flow through an arbitrary point is always conserved. "If the total in flow and out flow is not conserved there will be a net accumulation of fluid inside the cube". Mathematically we can write it as given in form of equation of continuity given in equation (3) [29];

$$-\nabla . J = \frac{\partial C}{\partial t} \quad ------ (3)$$

2.1.3 Fick's 2nd law

Fick's first law and equation of continuity can be combined to get the Fick's 2nd law So we can write as

$$\frac{\partial C}{\partial t} = \nabla . (D\nabla C) \quad ------ (4)$$

2.1.4 Random walk theory and atomic jumping

From the microscopic point of view, diffusion happens by the Brownian motion of constituting particles in the fluid, Einstein observed this and named this motion as chaotic motion of particles that are suspended in the fluid [1]. He argued that this motion is due to the Boltzmann distribution of energy to the individual particles that oscillate in action to this energy. Further this individual motion rises up collectively and result in the form of stochastic motions that occur through all the matter from macro scale to atomistic level. Einstein related the mean square displacement of oscillation to the diffusion constant D; this is known as Einstein Relationship. Einstein showed that particles in suspension under some concentration gradient will experience a force K given as, this will allow the particle to move under concentration gradient.

$$Kv = \frac{RT}{N}\frac{\partial V}{\partial x} \quad ------(6)$$

Or this could also be written as $D = \mu k_b T$ Here μ is known as mobility. While k_b is Boltzmann constant.

2.1.5 Random Walk

Diffusion in gases can be described as random motion of particles that flight freely before colliding among themselves. These well-defined path lengths are named as mean free path, this path is much smaller than the average atomic spacing in the structure. This is the cased of gases, while in liquids and solids atoms are arranged in more regular pattern then gases. Atoms in solids are fixed at specified atomic sites, it take energy and time to for each individual hoop to occur. The time that it takes for a single jump to occur can be found by Debye frequency, that give very small-time equivalent o 10^{-13}s. for better understanding we can divide the diffusion in two types. Firstly, individual jumps may be the consequence of lattice defects like, vacancies or interstitials, the jump length is equivalent to the lattice parameters. Secondly the diffusive jump could be related to the thermal initialization, and this is very accurately given by the Arrhenius law of activation energy, that could be given as

$$\Gamma_{A\to B} = \nabla exp^{-\nabla G/k_b T} \quad ------(7)$$

Here ∇ is the attempt frequency that is equivalent to Debye frequency. While ∇G is the Gibbs free activation energy. And kb is the Boltzmann constant. We can express this diffusion relationship with the help of different simple models as it is well explained in [31].

2.1.6 Random Diffusion Walk in a Crystal

When we discuss the random walk in a periodic crystal structure, it could jump to a specific distance equivalent to the distance between two consecutive atoms. this could be equal to λ, if the coordination number of crystal is give by z. then this jump will happen with a probability of 1 / z. because of this jump the total displacement covered can be given as eq (8-10)

$$X^2 = \sum_{i=1}^{n} x_i^2 + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} x_i x_j \quad ------(8)$$

$$\langle R^2\rangle = \sum_{i=1}^{n}\langle r_i^2\rangle + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle r_i r_j\rangle \quad ------(9)$$

$$\langle X^2\rangle = \sum_{i=1}^{n}\langle x_i^2\rangle + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle x_i x_j\rangle \quad ------(10)$$

2.1.7 Uncorrelated Random Walk or Memory Free Walk

During a random walk, every new step is independent of all the previous one. So, such a motion of ions in the crystal is name as uncorrelated random walk or memory free walk, any correlation effect to this random walk will be termed as correlation. Although the terms $\langle r_i r_j \rangle$ in the equation contains memory effects/correlation effects, but for each pair we find another pair equal but opposite in sign so the average value is zero. Means there is no net correlation in this transition.

So we can conclude that in a periodic crystal lattice there are only specified value off random jumps that are equal to the coordination number. For a jump distance "d" along x-axis, jump can be written as $\langle x_{random} \rangle = \langle nd^2 \rangle$. We can introduce the jump rate here by using the relationship (11)

$$\Gamma = \frac{\langle n \rangle}{Zt} \quad \text{------- (11)}$$

Using these concepts, we can understand the atomic jump in this process. in this way we deal with the rate of reaction using transition state theory. That is discussed more briefly in the incoming section. For further derailed discussion we may concern the book and reviews in the references [31-38].

2.2 Defects and diffusion processes

Point defects are present in crystalline solids and they are interesting because of their property to diffuse through crystal, acting as diffusion vehicle. A complete/defect free crystal sustain overall charge and mass neutrality. And it remains with the periodicity of the lattice. In pure metals a point defect is perfectly shielded by the conduction electrons and overall structure remains neutral, however in the ionic crystal a point defect disturbs the overall neutrality of the system. Frankel disorder and Schottky disorder are the examples of such type of disorder, and they ensure the complete charge neutrality of the system. In the semiconductors the point defects include the charge states in the band gap and in this way, it neutralizes the overall charge state [39-47].

2.2.1 Effect of Temperature

Diffusion coefficient depends upon temperature and this temperature dependence is given by the Arrhenius equation.

$$D_{A \to B} = D_0 \exp\left(\frac{-\nabla H}{k_b T}\right) \quad \text{------(12)}$$

Here D_0 represents frequency factor. And ∇H represents the activation enthalpy of the diffusion reaction., T is the absolute temperature and k_b is the Boltzmann constant. We can calculate the activating enthalpy of the diffusion reaction as

$$\nabla H = -k_b \frac{\partial \ln D}{\partial \left(\frac{1}{T}\right)} \quad \text{------(13)}$$

It corresponds to the negative slope of the Arrhenius diagram. So, Arrhenius diagram given in figure 1, is the straight line with slope $-\nabla H/k_b$.

2.2.2 Pressure dependence of Diffusion

Using the Arrhenius equation of diffusion, we can calculate the diffusion dependence on Pressure very easily. We can analyze the dependence of diffusion on the pressure by considering that the fact that Gibbs free energy strongly depends upon pressure and this varies with the change in pressure. This can be given as using thermodynamics per equations (13), (14)

$$\nabla G = \nabla H - T\nabla S \quad ------(13)$$

or

$$\nabla G = \nabla E - T\nabla S + P\nabla V \quad ------(14)$$

Here we can see activation energy(∇E) is linked with change in volume ∇V. Further, by thermodynamics

$$\nabla V = \frac{\partial \nabla G}{\partial P} \quad -----(15)$$

This can be termed as activation volume. There are three main parameters that are involved in the activation process. This include ∇E, ∇S, and ∇V.

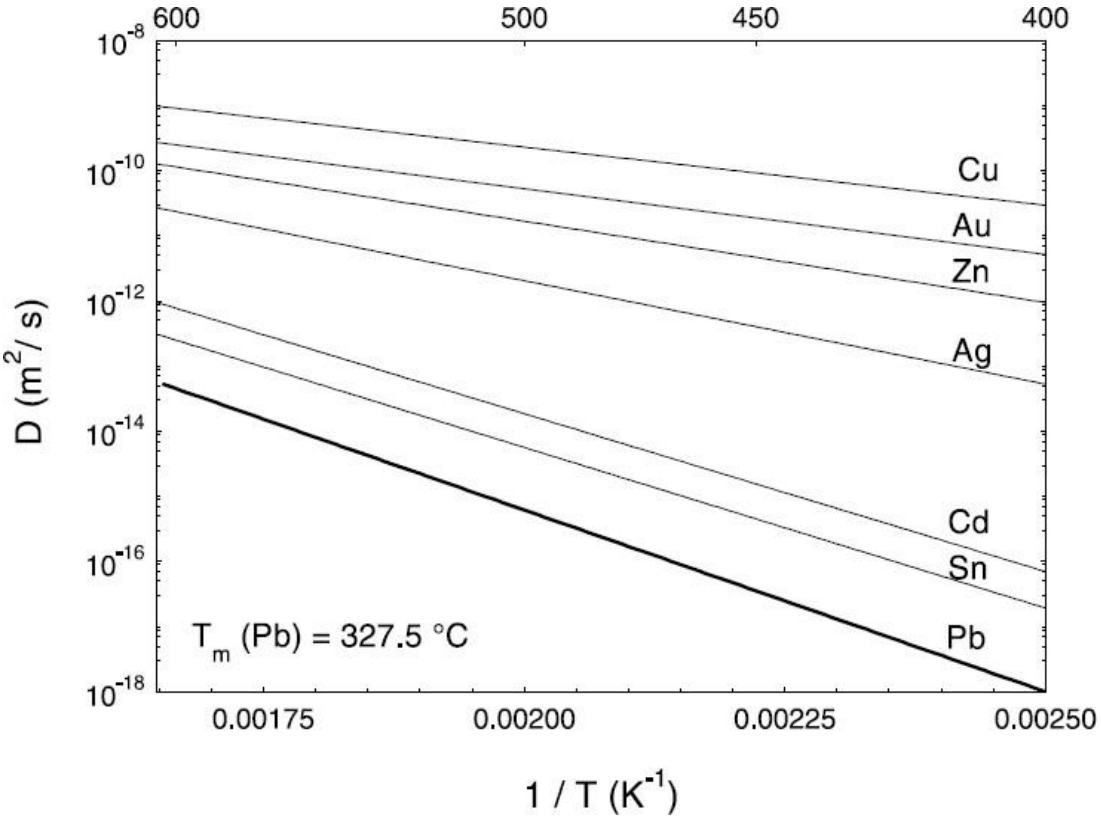

Fig. 1.: Arrhenius plot of diffusion vs temperature inverse for various elements [46, 47]. Enthalpy and activation energy are related through equation given below,

$$\nabla H = \nabla E + P\nabla V \quad -----(16)$$

In this equation the term $P\nabla V$ is high pressure term and it is neglected at low pressure. Effect of pressure in diffusion study is important. The knowledge of activation volume its sign and its magnitude provide the complete information about the diffusion process [48-53].

2.3 Diffusion and deriving forces

2.3.1 Diffusion mechanism

In previous studies LiFePO4 has been observed through molecular dynamics having two types of lithium hopping, a zigzag vacancy diffusion and Li-Fe andesite diffusion further it was observed that lithium diffusion is continuous process but discrete jumps that may be from one lithium site to another site available for migration or antisite i.e. Li-Fe [54-56]. Antisite hopping is slow process than Li-hop normally the 1-D across [010] channel.

2.3.2 Solid state Diffusion Mechanism

Movement of Li-ion and electron results charging and discharging of a battery [57] Energetic that influence charging/discharging is lithium insertion/extraction as a result charge-carriers/electrons also moves to neutralize the whole system. As common potential gradient technique works here, as Li-ion move toward low concentration electrons also move to maintain charge neutrality leading Li-ion diffusion. A simple reduction oxidation/reaction occurs while diffusion rate determines how fast a battery will charge and discharge. This diffusion of ions between electrodes is key factor of performance of a battery. Electrodes are always good conductor of both ions and electrons, electronic conduction can be enhanced by carbon coating or adding any of conductive material while ionic conductivity relates to structural composition of electrode from where ions can easily diffuse, It may be enhanced by creating defects in crystal lattice. Our focus here is ionic diffusion.

Diffusion of ions is categorized into two types macroscopic and microscopic. Macroscopic diffusion obeys Fick's law that is gradient of particular specie, it may be concentration gradient or chemical potential gradient i.e.,

$$J = -D\nabla C \quad \text{------(17)}$$

Where J, D, C, are flux, chemical diffusion coefficient and concentration respectively of particular specie. The chemical diffusion coefficient (D) here is counted as microscopic entity which can be calculated by TST

$$D = \frac{1}{6} a^2 \, v \, exp\left(\frac{E_a}{k_B T}\right), \quad \text{------(18)}$$

E_a is activation energy barrier, k_B is Boltzmann's constant, T is absolute temperature and v is vibrational frequency of Li-ion which is usually 10^{13} Hz. E_a is calculated by Nudged Elastic Band method. v is due to Brownian motion that is particle's frequency of vibration which increase with increase in temperature. As temperature is increased particle distort from its equilibrium position creating probability to cross the energy barrier. This type of motion is caused by two factors an empty adjacent lattice site (vacancy) or particle with sufficient energy that it can break bonds creating distortion in crystal (non-vacancy).

2.4: Calculation of chemical diffusion using NEB:

Computation methods are becoming the well-established and widely accepted tool for today research and they are helping a lot to experimentalists to save their time, sources and efforts. There are many of methods that are best adopted in each and every branch of science. E.g. Density functional theory is much successful in describing the electronic properties of materials. It relays on by using Schrödinger equation and solving Kohn Sham equation for many electron atoms. In theoretical condensed matter physics and computational chemistry, often we have to deal with the chemical transitions of atoms and molecules, this include calculating their rate of transition, calculation of

potential barrier that need to be overcome for a transition and study of diffusion events. Any of such event results in change of geometry and crystalline frame work. Generally, this change of configuration is obtained by solving Schrödinger equation; calculating all possible interaction between atoms and electrons. But we can also tackle this using Quantum Monte Carlo simulation or classically using molecular dynamics. Classical methods are much useful as they are computationally much cheaper than quantum methods.

3. Methods to find MEP and Transition Sate Theory (TST):

Crystal vibrations or phonons include the lattice vibration. From thermodynamics we know that each of such vibration or degree of freedom can be represented by $k_BT/_2$ here k_B is the Boltzmann's constant value 1.3807 x 10^{-23}JK^{-1} .

While dealing purely with Transition rates and finding transition states we focus on considering an energy surface of N atoms from an N atom configuration where transition is taking place between two consecutive energy minima thus describing one complete transition. This path will be the minimum energy path (MEP) for this transition. Both of these energy minima will share a common energy maximum that is named as saddle point, as shown in fig.

Transition state theory is based on model how a reaction takes place at molecular level. It generally deals with the reactions that proceed by continuous change in their relative positions and potential energy of the reactants. Let's assume a general reaction

$$A + BC \rightarrow AB + C \quad ------(19)$$

This reaction has rate constant k. The energy profile for such reaction is given in figure 2.

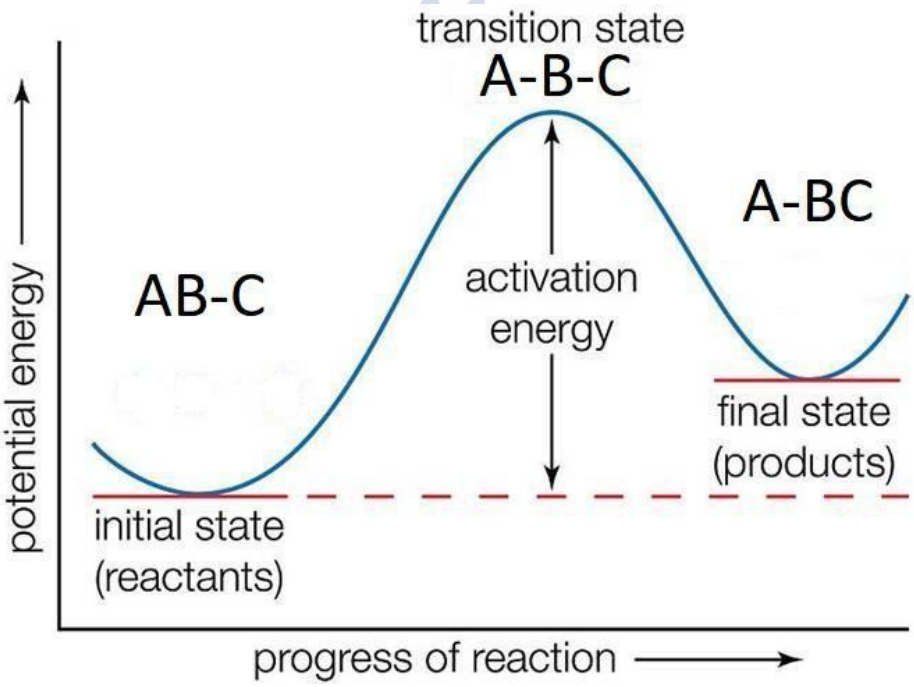

Fig. 2: Pictorial representation of Transition State Reaction The complete reaction will be like

$$A + BC \rightleftharpoons ABC \rightleftharpoons AB + C \quad ------(20)$$

From the reaction and the energy profile we can see that there is high energy configuration or pre-equilibrium state between two minimum energy states. This intermediate state ABC is also

named as Transition state or activated complex. The difference of energy between the initial state and intermediate state is also known as activation energy that is required for any practical transition to happen. This path between initial to final state is known as minimum energy path.

If we want to relate this process with an example then we can consider the adsorption of any atom say Lithium on a Cu surface. If we put the atom on the surface and relax the whole system made an energy plot for Li atom, we will see Li atom will face an energy barrier before getting another equilibrium state. This high energy point between two energy minima on the energy graph will represent the transition state. This is also known as saddle point or Bridge point between two equilibrium states.

This minimum energy path is very important as it describes the mechanism of the reaction and it tells, and by calculating the energy barrier we can calculate the reaction rate for a chemical reaction [58]. Usually this minimum energy path is obtained by constructing an energy surface of N atoms with each having specific coordinates E ($R_1, R_2, R_3, R_4 \ldots, R_N$) and related energy points on the surface given by $E_1, E_2, E_3, E_4 \ldots, E_N$. The minimum energy path will be the set of coordinates b which a configuration of atoms moves from one energy minima to other without passing through any other minima. Although there are infinite number of paths that connect these two equilibrium states but one that had key role in the transition will be the path that minimizes the change in energy during this reaction. An example of energy path is shown in figure 3, that has been calculated for the Li ion hooping between the channel and across the channel for silicon crystal in the presence of strain along the layers.

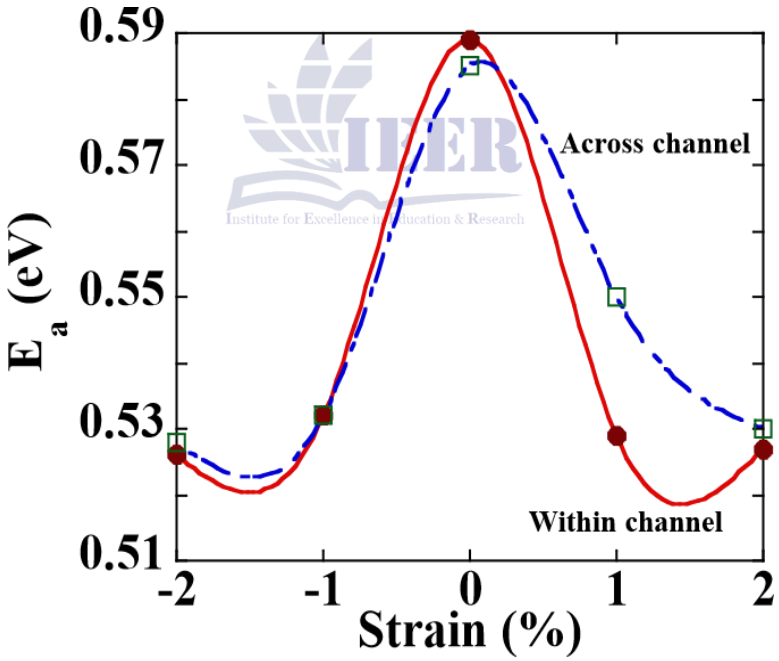

Fig. 3: Transition path of Li ion hooping in the bulk Silicon, showing the activation barrier of Li ion hope [59].

1. Calculation of the rate of chemical reaction using TST:

We can use the concepts from statistical mechanics to compute the transition rate of reaction. The average energy accessible to each degree of freedom is given as $k_BT/2$ at room temperature is given by 0.013 eV, this is the energy contained by particle in the material, in a real thermodynamic system as an atom moves, it feels number of other forces from its environment and nearby atoms. So, the energy of moving atom will increase with time, till it manages to cross the energy barrier, we can define the energy

barrier as the difference of energy between the highest and lowest energy point. Here we predict an important rule about TST, we can get the useful information from the TST only in the cases where energy required for a chemical process is considerably larger than the average thermal energy related with each degree of freedom, as we won't be able to mimic the energy of transition with the thermal energy.

In order to calculate the rate of transition between states A to B as shown in the figure, we can calculate the rate of hooping using given formula.

$$K_{A-B} = \frac{1}{2} \times (V_{avg}\ Hooping\ atom) \times (Probability\ of\ atom\ at\ Saddle\ point) - - - (20)$$

Probability is given for all possible positions of atom in their initial

$$P(x) = exp - [\frac{E(x)}{KBT}] - - - - - - (21)$$

From statistical mechanics we can write the probability for finding the transient particle at the transition state x^t

$$x = x^t = \frac{e^{-\beta E(x^t)}}{\int_A e^{-\beta E(x)} dx} - - - - - - (22)$$

While thermal velocity of transient atom can be given as

$$V_{avg} = \sqrt{\frac{2}{\beta \pi m}} - - - - - - (23)$$

By using the all value in the main equation, we get the rate constant,

$$k_{A \to B} = \frac{1}{2} \sqrt{\frac{2}{\beta \pi m}} \frac{e^{-\beta E(x_t)}}{\int_A e^{-\beta E(x)} dx} - - - - - - (24)$$

1.1 Energetic in TST based diffusion mechanism:

The integral in the denominator makes situation a bit complex, we can simply this by using the concept of zero-point energy, for describing energy at the starting position $E(x_A)$, as thermal energy at this point is not enough to perform considerably vigorous oscillations.

This shows quantum mechanical solution of minimum energy of any Harmonic vibrating particle given by its Taylor expansion,

$$E = E_0 + \frac{k}{2} x^2 - - - - - - (25)$$

And for the above case it will be

$$E(x) = E_A + \frac{k}{2} (x - x_A)^2$$

$$\int_A e^{-\beta E(x)} dx \cong e^{-\beta E A} \int_A e^{-\beta \frac{k}{2}(\bar{x} - x_A)} dx \quad -----(27)$$

$$-----(26)$$

While calculating the energy at the starting equilibrium position x_A, we have to calculate the energy on all real line. So, we give the limits of integration from $-\infty$ to ∞, and solve this integral in the form of Gamma integral that have solution in the form of square root.

$$\int_{-\infty}^{\infty} e^{-\beta E(x)} dx \cong e^{-\beta E A} \int_{-\infty}^{\infty} e^{-\beta \frac{k}{2}(x - x_A)} dx = \sqrt{\frac{2\pi}{\beta k}}$$

$$e^{-\beta E A} \quad -----(28)$$

While ground state vibrational frequency of oscillator can be given as $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$. That can also be written as $\sqrt{\frac{2\pi}{\beta k}}$, using in the rate equation we get,

$$k_{A \to B} = \nu exp \frac{E - E^{\dagger}}{k_b T} \quad -----(29)$$

This is the relation that gives the rate of reaction from initial position to final position. And we will use this relation in the NEB method to find the rate of any transition. This could be a reaction, a simple transition of Li+ or Na+ in their respective batteries, or it could a simple hoop of atom or electron while diffusion on a surface, we can describe any reaction on this theory and can find the rate of reaction, in that respective transition to calculate the quality parameter of that material like diffusivity, and then power density etc. one of its application is the Arrhenius rate equation that is well known to determine the diffusion process. The factor $E - E^{\dagger}$ gives the difference of energy in that hoop and we can say it the migration barrier for that transition. Since we used the harmonic approximation while its derivation, like we used in equation 4 and 5 we used this concept that's why this theory is also called Harmonic Transition state theory.

1. Elastic Band Method:

Now after guessing that we can calculate the rate of reaction using first principle calculations, we try to find out a method that could be used for this purpose, we are bounded to calculate the minimum energy and transition state to find the rate of reaction, this is so important to find the rate of reaction for a reaction ,that especial numerical methods have been developed for this purpose as We can't use DFT based iterative minimization methods to find the Transition state as they generally move downhill to find the minimum energy state.

The method that is mostly commonly used to

find the Minimum energy path on the Potential energy surface (PES) is Nudged Elastic Band method; this method is the improved form of the old chain of states of method where a series of local minima's or string of images is used to define and energy path between two minimum energy states. An illustration of such path is presented in the figure we can see there are 8 independent points along the path having respective set of coordinates that shows 8 stages of the system evolution where Energy calculation will be done on each image using DFT method. Since these points are connected by the spring forces so all the points must have force between them given by

$$F = -\Delta E(r) - - - - - -(30)$$

We can analyze all the images except 0 and 8 have this force between them while the initial and final state has no forces between them as they reside on the global minima's. A path defined in this way will be termed as Minimum Energy path or MEP. We can conclude this that a path defined by an Image will be MEP only if the forces defined by this reside only along the path (the force vector shouldn't make angle with the initial path).

Elastic Band method has the reason for its name; these images are connected by equal spring forces that ensure the constant distance between any two consecutive states and thus continuity of the path that's why this is called Elastic Band method. Since these images have to take the minimum energy and they have harmonic elastic between the images, mathematically we can give an equation for the model give in the figure using the equation no 3, that incorporate the both of the requirements given by

$$f(r_1, r_2, r_3, \ldots\ldots\ldots, r_8) \qquad \underline{k} \qquad 2$$

$$min \quad {}_7 = \sum_{i=1}^{8} E(r_i) + \sum_{i=1}^{8} {}_2 (r_8 - x_0) \quad - - - - - -(31)$$

This equation incorporates all the desired conditions; we couldn't see function value at r_0 and r_8 as these two images are fixed at the stable low energy configuration. Minimization of this function will give us the MEP for the transition from 0 to 8

1.1 Nudged Elastic Band Method (NEB):

Nudged Elastic Band method is the improved form of elastic band method; here we introduce a correction to adjust the set of images towards MEP. This is done by introducing a direction vector between two images that is resultant of two vectors$F^{\perp}$ and $F^{|}$, this is known as force projection scheme that include two forces one that act parallel to the images call spring force and the other that act perpendicular to the images is called potential force,

We define a path between two images that minimizes the path, the mathematical logic we present is given as. Every component other than one that is not pointing along the direction of MEP must go to zero. That is given as

$$F_q^{\perp} = F_q - (F_q \cdot Q)Q = 0 - - - - - -(32)$$

The solution we understand from this equation is that each image have to do a downhill movement along the path that is produced by the$F^{\perp}$, since the method is called the elastic band method so we have to include the spring forces or harmonic spring in the process, to ensure the path along MEP at downhill direction in this way we can define the elastic band method by taking the resultant force at a point q, that determine the path of the transition, mathematically we can write it as

$$f_q = F^{\perp} + F^{Spring} - - - - - -(33)$$

$q \quad q$

The spring force that acts along with F act all the way on the PES, but our desired components of this force F^{Spring} are only along the path that are in the direction of MEP or these are parallel to MEP so that we can write the spring force as $F^{\parallel}_{q,Spring}$. The equation becomes $f_q = F^{\perp}_q + F^{\parallel}_{q,Spring}$.

That is working scheme of NEB a more generalized description of NEB is given below

1.2 Schematics of NEB

The schematics of NEB is described below,

1. An NEB calculation follows a predefined (manually defined by the user) set of coordinates (images) to find the minimum path of a transition on PES. These images basically guide the calculation to the MEP. The NEB is the follows iterative minimization scheme so the convergence rate will strongly depend upon the initial set of coordinates, a close estimate to real MEP will instantly guide the calculation to MEP
2. Working of NEB is based on force projection scheme where potential energy forces by the system act perpendicular and spring forces act parallel to the path.
3. By increasing the no of images will result in more complete description of MEP and more complete picture of MEP however this increased accuracy is compensated on the expenditure of more computation cost.

This is the generalized scheme of NEB working, however depending upon the system on which NEB is to be performed, and the complexity of force projections, e.g. if you want to check out the Li ion transition in the crystalline environment of LiFePO4, with orthorhombic structure and a complex transition pathway, we have to vary the computational recipe to complete the calculation and find out the real MEP, this may include , trying different initial path to get the accurate estimate and using spring forces with variable strength. But the overall result should be to Find the real MEP and the rate of the transition.

1.3 Calculation of Li ion Diffusion mechanism using NEB

Here are some examples of diffusion studies and their analysis based on NEB.

1.3.1 Study of Diffusion in Silicon

Strain effects on lithium diffusion, [59] pure Silicon in cubic structure was studied by Paramita and Abhijit, Since silicon is very active anode material in Li ion batteries having theoretical capacity of 4200 mAh g-1, irrespective of this high capacity pure silicon face problem of volume expansion on Li delithiation and lithiation , To understand the chemical phenomenon involved in this expansion climbing Nudged Elastic Band (Cneb) study has been performed in the presence of vertical strain. They studied the interatomic interaction between Li-Li, Li-Si and Si-Si by modeling interatomic potentials using 2NN modified embedded atom method (MEAM).

They found that Li ion moves from one tetrahedral site to another tetrahedral site through intermediate Si atom, on compares the cNEB energy profile for Li ion diffusion in the material, it was seen that Li ion hooping is not concerned with Li ion concentration within the channel as can be seen in the figure 3.

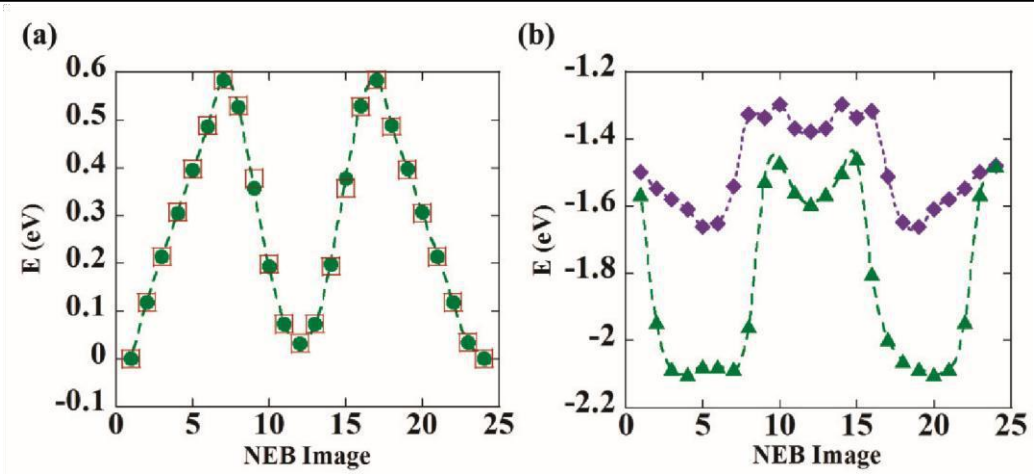

Fig. 4: (a) denotes activation energy in case of single Li-ion diffusion, circles and squares represent within and across the channel diffusion respectively (b) activation energy in the presence of another Lithium atom; diamond and triangles represent within and across the channel movement respectively.

since both energy diagram are in exact match for both energy cases. While across the channel movement (movement with the path across the unit cell boundry) depends upon the neraby Li ion as the activation barrier increases considerably with the presence of Li ion. It was seen presence of Li ion introduces the saddle point between two equilibrium states, the number of saddle points increases as we increase the no of Li ions in the pathway. This dramatic behaviour was considered due to the strain by the nearby Li ion in the structure,. They further verify it by applying biaxial strain on the srturcture and they found that Activation barrier increase with the increase of strain by 0.05 eV and this affect the rate constant to a factor of 10. It was concluded that this energy change in MEP is due to stretching and compression of Si-Si bond [60, 61].

1.3.2 Diffusion in Vanadium doped LiFePO4

Study has been performed on vanadium doped LiFePO4 using NEB method [62] In both intrinsic and doped form lithium ion tends to move in 1-dimension. It has been revealed that diffusive activation energy barrier has been reduced by vanadium doping significantly that result in high carrier mobility and thus contributes in better electrochemical performance of the battery. The decrease in barrier height and the diffusion path has been shown in Fig.5.

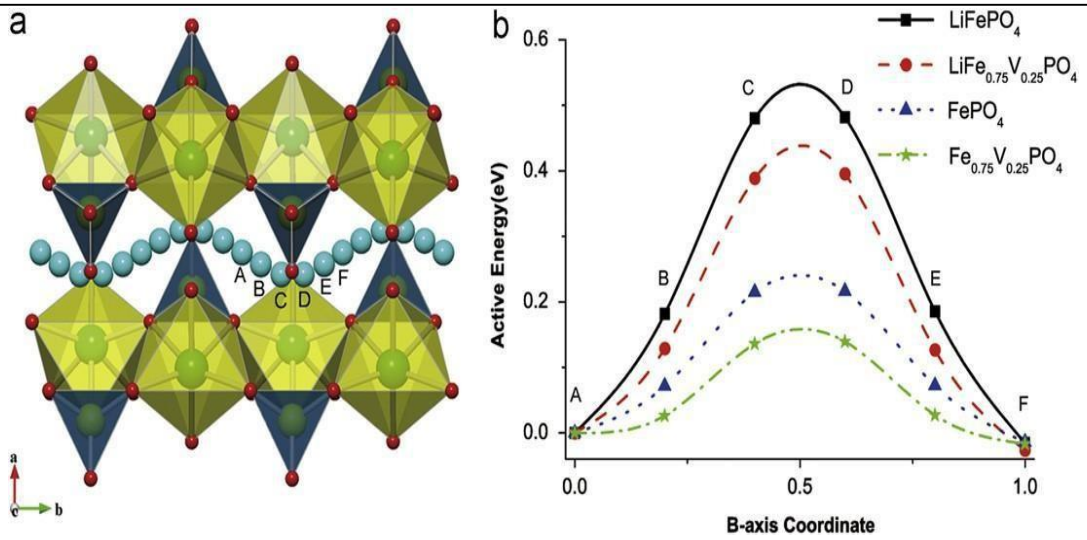

Fig. 5 (a) Diffusion of lithium along b-axis (b) activation energy barrier due to doping

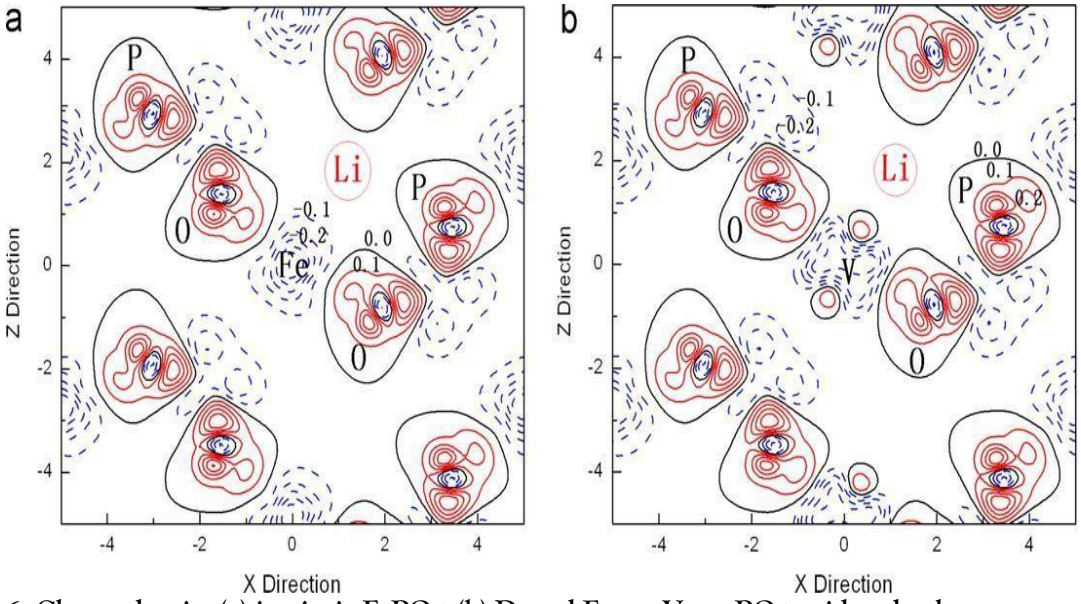

Fig.6: Charge density (a) intrinsic FePO4 (b) Doped Fe0.75V0.25PO4 void and volume expansion

This happens due to the increase in 4.5 % volume of the structure. This volume expansion creates voids in the super cell and thus favors the Li ion diffusion; this thing was also verified by the charge contours Fig. 6. however, this volume expansion was not severe enough that it results in destabilization of crystal structure [63, 64].

1.3.3 Diffusion study in Li2CO3

Lithium-ion diffusion mechanism in Li2CO3 has been studied by H. Iddir using DFT calculation, Li-Ion from adjacent sites moves to interstitial sites [65]. The equilibrium position form dumbbell interstitials that are two interstitial Li^+ at the same place. They calculated the diffusion path of li-ion through large open channel and small open channel having energy barrier of 0.28ev and 0.60ev respectively. Large open channel has the migration path of [010]. It is not straight forward but has its zig zag path forming energy diagram as shown in fig 7.

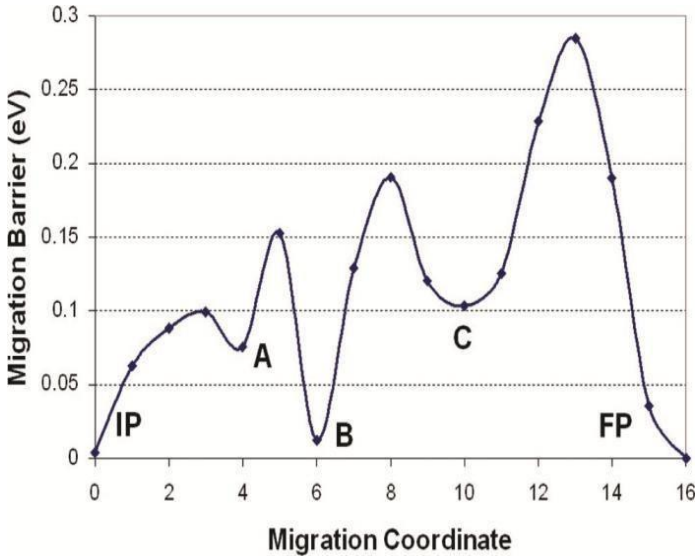

Fig.7: Migration barrier of 0.28eV through large open channel [010]

From figure 7, we can see that energy varies in a sinusoidal pattern. At the initial position the peaks are not very sharp showing little migration energy for hopping but at the last hoop C-FP has migration barrier of 0.28ev which is due to bond formation and breaking with the oxygen atom, as at this position Li is highly coordinated with the oxygen atoms. In the small open channel hoop Li ion does not follow a straight path but it moves across the channel through $CO3^{-2}$, this has the energy barrier of 0.60 eV.

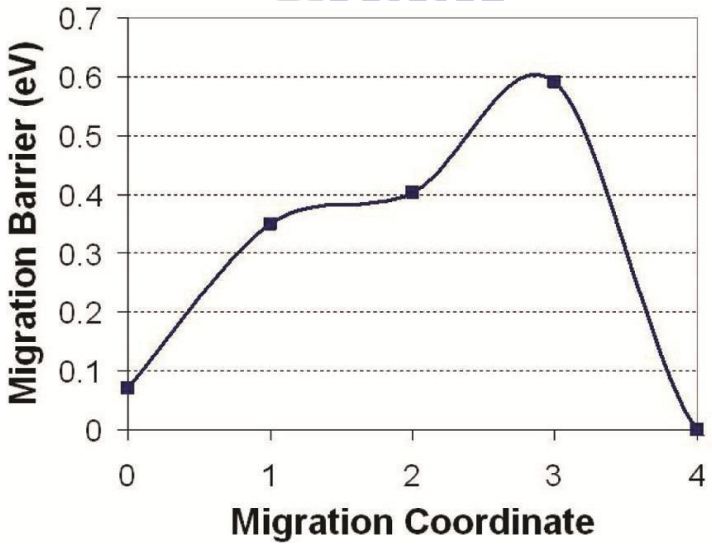

Fig. 8: migration barrier of 0.60 eV along small open channel

They also calculated the Diffusion of Li atom in the structure as it happens due to the Li ion recombination with the electron. And any vacancy causes the Li atom to hoop. This mechanism of hooping has large migration barrier as Li atom carries positive charge and attracted by negatively charged oxygen to form ionic bond that result in large diffusion barrier and make the mechanism tough to happen as given in fig 8 [66-68].

1.3.4 Diffusion study in family of Olivine Phosphate materials

Mobility of lithium in olivine phosphate materials was investigated by D. Morgan [69]. They briefly describe that lithium diffusion depends on electronic conductivity of the cathode further they also applied Nudged Elastic Band Method to find lithium hopping in olivine family LiMPO4 (M=Fe,Mn,Co,Ni). Lithium adopts three different paths for transport,

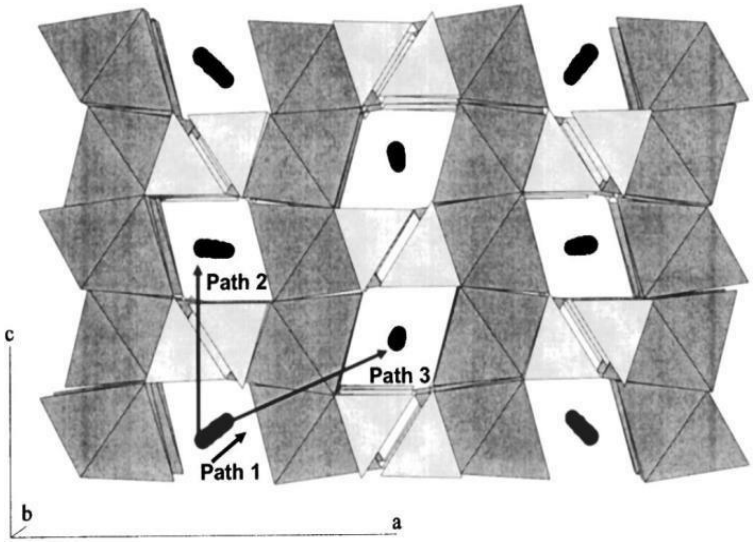

Fig.9: Olivine structure is shown in which dark gray are Fe octahedral, light gray are P on tetrahedral sites and blacks are Lithium while lines show Li-ion diffusion path.

Path 1 is one dimensional lithium hooping across one octahedral site to other octahedral site (figure 9) through tetrahedral site having lowest energy barrier. Lithium hoop across path 2 is from octahedral site to octahedral site through intermediate octahedral site having face sharing with P at tetrahedral site, this has energy barrier greater than 2.5eV which is much greater than path 1.

Along path 3 Lithium has to migrate through face shared tetrahedral and octahedral sites with Fe and P cations, which require a large energy barrier to overcome of about 1eV. So, lithium-ion conductivity through path 2 and path 3 is negligible. Lithium transport is mainly due to path 1, which is 1-dimentional lithium movement. Here ionic conductivity is greatly affected by the presence of neighboring P atoms presents at tetrahedral sites or any defect in the path of lithium migration.

1.3.5 Diffusion study in N doped LiFePO4

It has been reported that Li-ion diffusion in LiFePO4 can be increased by nitrogen doping as sketched in figure 10 [70].

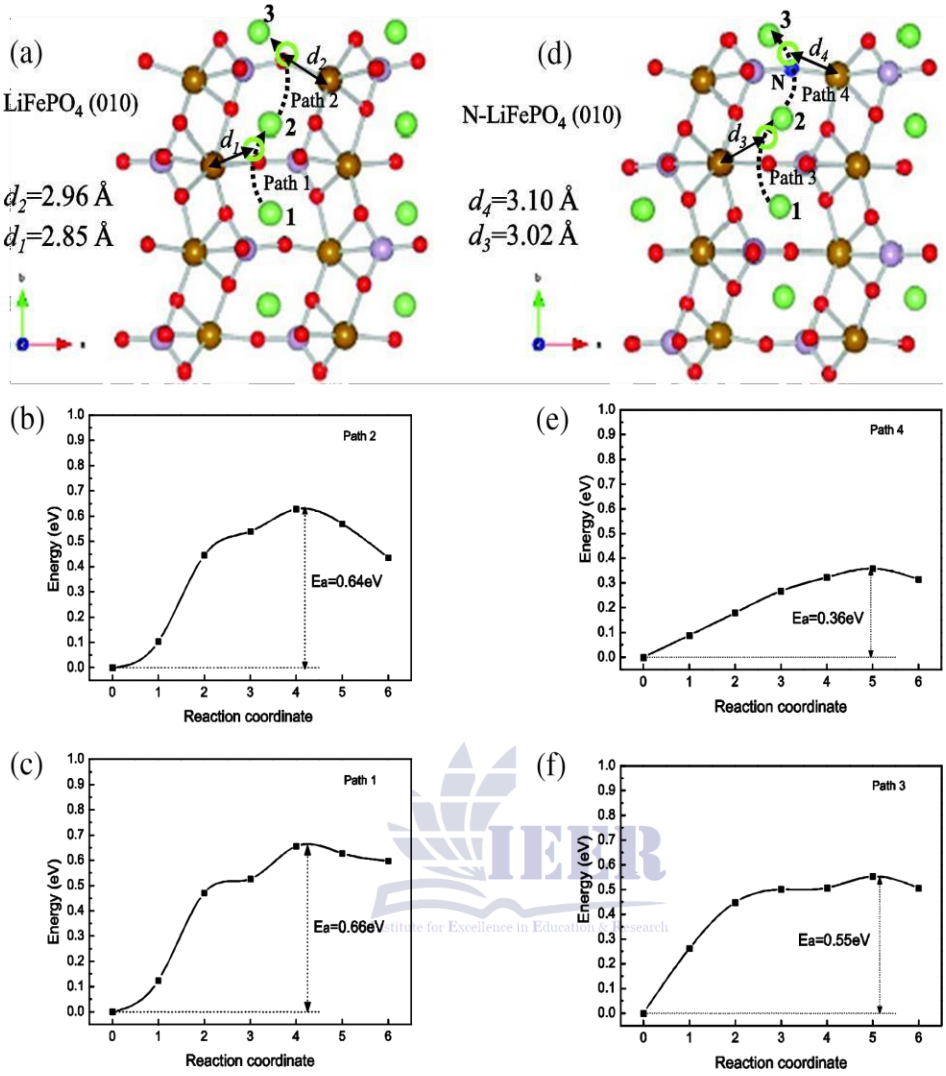

Fig.10: (a) Optimized structure of LiFePO4 (b) activation energy barrier for LiFePO4 (c) N-LiFePO4 with increased distances between sites (d) activation energy barrier for N-LiFePO4

They used NEB Method to compute the barrier for activation energy for intrinsic and N-doped LiFePO4. They reported band gap of N-doped LiFePO4 is much less than intrinsic bulk LiFePO4 and LiFePO4; 2.93 and 0.73 respectively less than N-doped LiFePO4 and hence there is low activation energy barrier of about 0.36eV. This low energy barrier will result in greater diffusivity of Li-ion. They further explained that this increase in diffusivity is due to increase in distance between sites for Li hopping of LiFePO4. Which lower the electrostatic repulsion between Li-ion and Fe-ion at transition state by lowering the activation barrier and hence greater diffusivity.

1.3.6 Diffusion study in LiCoO2

Xiao Gu at al. investigated feasibility of LiCoO2 using nudged elastic band method in which they extracted that LiCoO2 may work better for liquid electrolytes having pH 11 or greater otherwise hydrogen atom will diffuse to intercalation sites (figure 11) as a result cycling will be reduce [71]. As lithium atom diffuse to

nearby vacancy by crossing an energy barrier of 0.37ev while hydrogen need only 0.32ev which is favorable to hydrogen atom.

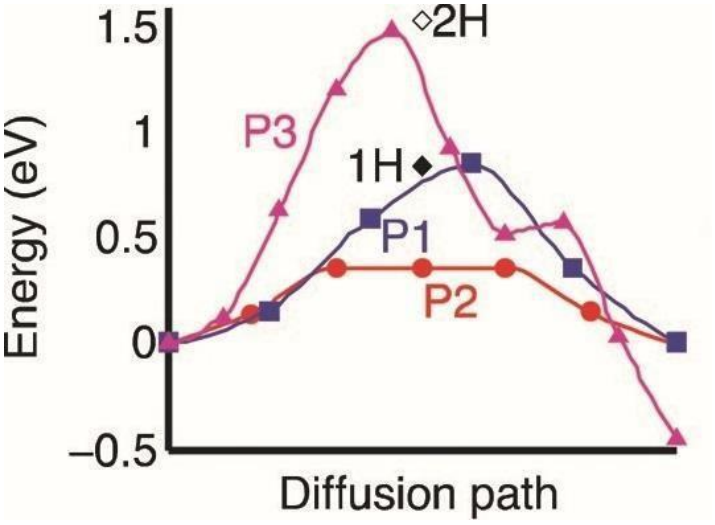

Fig.11: Different diffusion path are adopted by Li-ion; corresponding energy barrier for Li-ion are shown, P1, P2 and P3. P1 and P3 give higher energy barrier due to involvement of 1 and 2 H-ion respectively in the diffusion tunnel path, P1 show direct diffusion of Li-ion without involvement of hydrogen ion [71]. Reprinted with permission from American Chemical Society.

As a result, total capacity of system will decrease. Further they found that if hydrogen will intercalate to lithium sites than Li-ion has to cross energy barrier of 0.80 eV and even greater up to 1.50 eV.

1. Summary:

We have presented a simple and straightforward elaboration of resourcefulness of Nudged Elastic Band (NEB) method to understand the solid-state diffusion mechanism in ceramics for application in lithium ion batteries. The basics of diffusion in solid state materials, the causes of diffusion, how defects are important in this process and the effect of temperature and pressure on solid state diffusion are described in detail. The description is prepared by shed light on implementation of this method using simulation and computational tools to investigate the mechanism of solid-state diffusion. The writeup was planned by considering different backgrounds of the readers. Further, insights into climbing Nudged Elastic Band method (cNEB) are also given in order to ensure the complete picture of the mechanisms involved. A few examples have been given to show how this method is adopted to model the diffusion mechanism in various solid environment.

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