ABSTRACT

DHIMAN, PANKAJ. Dislocation Based Stresses during Electrochemical Cycling and Phase Transformation in Lithium-ion Batteries. (Under the direction of Dr. Hsiao-Ying Shadow Huang).

Defects in materials are inevitable: Formation of defects are due to that all processes are almost always far from equilibrium and take place at finite temperatures (>0 K). Defects in materials have been considered a nuisance until people realized how the defects can actually be used to alter the properties of materials as per need. Doping of material with alien atoms is a basic example of how the defects can be engineered to improve the properties. Defect engineering which involves manipulating the type, concentration, spatial distribution, or mobility of defects within a crystalline solid has become much more sophisticated in recent years, driven by the need to control material properties at small length scales. Electrode materials for lithium-ion battery like lithium iron phosphate (LiFePO_4) also contains defects that may be formed during charging or discharging at a finite temperature. The atoms in a lithium iron phosphate crystal containing a linear defect called dislocation are displaced from their perfect lattice sites and the resulting distortion produces a stress field around the dislocation. The present study deals with these mechanical stresses around dislocations in lithium iron phosphate and the change in stress field during phase transformation of lithium iron phosphate (lithium-rich phase) to iron phosphate (lithium-poor phase). A model consisting of multiple dislocations inside a lithium iron phosphate material incorporating anisotropic material properties is used to calculate stress fields using linear elastic theory and superposition method. The stress fields around dislocations during phase transformation of lithium-iron phosphate to iron phosphate are numerically simulated using Mathematica (Wolfram Research, Champaign, IL) incorporating the anisotropic properties of the material. The change in scan-rate dependent electrochemical behaviour of material due to change in stress field during

phase transformation from lithium-rich phase to lithium-poor phase is also studied, where a modified electrochemical kinetics equation (i.e., Butler Volmer equation) is derived and used to simulate the reversible cyclic voltammogram of the lithium iron phosphate using MATLAB. The results shows the stress inside material does not remain constant during phase transformation and its variations are dislocation orientation dependent. In addition, the result also shows that the presence of stress fields around dislocations changes the electrochemical behaviour of the material as suggested by the shift in the cyclic voltammograms. The effect of increasing scan rate on cyclic voltammogram is also studied for lithium iron phosphate. The results show that the increase in current at peaks is independent of the orientation of dislocations studied. Moreover, the decrease in current corresponding to a particular overvoltage value before anodic peak and increase in current after the anodic peak is found to be somehow proportional to the scan rate. Increased scan rates show increased deviation of current from a cyclic voltammogram for material in which there is no phase transformation. The results provide an insight into how presence of defects and phase transformation changes the electrochemical behaviour of the material. It is concluded that the combined effect of the stresses induced around dislocations during phase transformation and high scan rate can be used for creating batteries for specific applications based on the overvoltage encountered in those applications. The present study incorporates electrochemistry, defects and phase transformation into one battery chemistry and thus is important in our understanding of the Li-ion batteries.

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Dislocation Based Stresses during Electrochemical Cycling and Phase Transformation in
Lithium-ion Batteries

by
Pankaj Dhiman

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DEDICATION

To my parents and brother

None of this would have been possible without you.

Thank you for always being there and supporting me.

BIOGRAPHY

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CHAPTER 1: INTRODUCTION

1.1 Lithium Ion Batteries

Increasing world population along with rapid urbanization and human reliance on technology has resulted in substantial increase in the energy demand worldwide in recent years. The U.S. Energy Information Administration's latest International Energy Outlook 2017 (IEO2017) projects that world energy consumption will grow by 28% between 2015 and 2040 as shown in Figure 1.1: .

Figure 1.1: World energy consumption by energy source.

Petroleum based fuel sources have been used since starting of industrialization to meet the energy requirement worldwide but has caused major environmental issues including global warming and thus cannot be relied upon for meeting ever increasing energy demands in future. As the carbon dioxide emissions from transportation exceeded those from the electric power in year 2016 [1] as

shown in Figure 1.2: , the need for a promising energy storage solution in future automotive industry emerged.

Figure 1.2: Carbon dioxide emissions by sector, Dec 1973-May 2016.

Lithium ion batteries having high gravimetric and volumetric energy density [2] have made possible the realization of electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug in hybrid electric vehicles (PHEVs) reducing harmful environmental effects of internal combustion engines. A comparison of different battery types in terms of energy density and power density is shown in Figure 1.3: and it reveals the superiority of Li-ion batteries in development of EVs, HEVs and PHEVs. Due to their high energy density, lithium ion batteries are also being used excessively in portable electronics including mobile phones and laptops.

Figure 1.3: Schematic representation of different secondary batteries in terms of power density and energy density [2].

1.2 Lithium Iron Phosphate as electrode

There are many cathode materials available for usage in lithium ion batteries with their own advantages and disadvantages. Lithium Cobalt Oxide (LiCoO_2) is utilized in most portable electronics as the cathode material due to its high energy density [3] but possesses safety risks [4] due to cobalt being toxic and LiCoO_2 having low thermal stability [5]. Thus, LiCoO_2 batteries cannot be used in electric vehicles (EVs) where safety is a major concern. Overcoming the limitations of LiCoO_2 , an alternate cathode material was proposed by Goodenough in 1996 [6]. Despite having lower energy density than LiCoO_2 does, lithium iron phosphate also known as LFP is a highly commercial used cathode material because of its longer life cycle, thermal stability, flat

discharge voltage (~ 3.6 V vs Li^+/Li^0) and low price. Lithium iron phosphate also avoids the environmental concern related to cobalt entering environment through improper disposal of LiCoO_2 . Despite all these advantages, lithium iron phosphate suffers from low electrical conductivity [7]. However, electrical conductivity of lithium iron phosphate is shown to improve by doping of lithium iron phosphate with alien atoms, surface coatings or changing crystal morphology [8]. Characteristics of lithium iron phosphate such as high energy density and environmentally safe accompanied with long life cycle thus makes it a promising cathode material that has already been exploited in the batteries.

1.3 Research Objective

Defects in materials are inevitable. Formation of defects are due to that all processes are almost always far from equilibrium and take place at finite temperatures (>0 K). For longest period of time, defects in materials have been considered a nuisance until people realized how the defects can actually be used to alter the properties of materials as per need. Doping of material with alien atoms is a basic example of how the defects can be engineered to improve the properties. Cathode materials like lithium iron phosphate also contains defects that may be formed during charging or discharging at a finite temperature due to a number of reasons. Many research has already shown how defects in lithium iron phosphate can be engineered to control material properties. Li et al. [9] evaluated the coupled effects of surface and dislocation mechanisms on diffusion induced stress in spherical nanoparticle electrode. They showed that the tensile stresses in spherical electrode are weakened by the coupled effect and even converted from tensile to compressive. Thus the effect was considered useful suppressing cracks nucleation and propagation caused by the internal damage during battery charging and discharging cycles. Li et al. [10] analytically modelled the

effect of dislocations on diffusion induced stresses in a cylindrical lithium ion battery electrode. They explained the combined effect of diffusion induced stresses and dislocations on preventing the crack nucleation and propagation under galvanostatic or potentiostatic conditions. Ulvestad et al. [11] studied the topological defect dynamics in operando battery nanoparticles using Bragg coherent diffractive imaging and reported the nucleation of lithium rich phase near the dislocations during the structural phase transformation. They also found out the material elastic properties to be considerably different from the bulk (*i.e.*, negative Poisson's ratio) in the vicinity of dislocations at high voltage. The research supported the idea that dislocations can be used to tailor material properties. The aim of this research is to study the dislocation-based stresses inside lithium iron phosphate during electrochemical cycling and phase transformation. The work is continuation of the work done by Huang and Wang [12] in which a mechanism for the generation of dislocations in lithium iron phosphate cathode during charging and discharging of the battery was suggested. The research provides insight on how the stresses around dislocation changes during phase transformation of the lithium iron phosphate. The change in electrochemistry of material due to the stress changes during phase transformation is also studied. The present study incorporates electrochemistry, defects and phase transformation into one battery chemistry and thus is important in our understanding of the Li-ion batteries.

CHAPTER 2: LITERATURE REVIEW

2.1 Electrochemical Principal of a Lithium Ion Battery

A lithium ion battery works on the simple phenomenon of transferring lithium ions from positive electrode to negative electrode during charging and vice versa during discharging. Lithium ion batteries are rechargeable batteries that restore their charge when electrical energy from outside source is supplied causing the reversal of negative to positive electron flow that occurs during discharging. The anode used in most Li-ion batteries is generally made up of graphite while lithium metal oxides such as LiCoO_2 (Lithium Cobalt Oxide) or LiFePO_4 (Lithium iron phosphate) is generally used as a cathode material. The use of a lithium containing salt enables the transportation of lithium ion from one electrode to the other while simultaneous transfer of electrons also takes place between the electrodes.

Figure 2.1: shows the charging and discharging process of a lithium ion battery where graphite is taken as anode material and a lithium metal oxide is taken as a cathode material. The negative material is reduced, and positive material is oxidized during charging and vice versa occurs during discharging.

Figure 2.1: Schematic of the charge/discharge process in a lithium-ion battery [13].

The reactions taking place at the positive electrode and negative electrode during charge and discharge are given by Equation 2-1 and Equation 2-2

The overall reaction taking place is given by the Equation 2-3.

2.2 Cathode Materials

The specific advantages and disadvantages of LiCoO_2 and lithium iron phosphate as cathode materials were discussed in section 1.2 as they both have been used commercially in the past. Yet another cathode material overcoming the limitations of LiCoO_2 and being a successful contender is the Lithium Nickel Manganese Cobalt Oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) commonly known as NMC. NMC has potential applications in automobiles including electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug in hybrid electric vehicles (PHEVs). The improved electrochemical performance of NMC is achieved by partially replacing the cobalt in LiCoO_2 by Ni and Mn [14]. The cost is also reduced at the same time because of replacement of expensive cobalt. NMC offers high power and energy densities along with good thermal stability. As such specific properties of NMC can be tailored by changing the composition of nickel and manganese. NMC is a much newer material than lithium iron phosphate and much of the research are required to use it in batteries to its full potential. The crystal structures of NMC and lithium iron phosphate has been discussed in the following sections.

2.2.1 Lithium Iron Phosphate

2.2.1.1 Crystal Structure of Lithium Iron Phosphate

Lithium iron phosphate (LiFePO_4) is the most commonly used cathode material in lithium ion batteries (LIBs). Lithium iron phosphate (also known as LFP) has an olivine structure in which one iron atom and six oxygen atoms form an octahedral coordination sphere and one phosphate atom and four oxygen atoms form a tetrahedral. The 3D network consists of FePO_6 sharing O corners. Lithium mobility is provided by infinite 1-D tunnels of lithium sites. Lithium iron phosphate belongs to orthorhombic P_{nma} space group with lattice constants $a=10.334 \text{ \AA}$, $b=6.002 \text{ \AA}$ and $c=4.695 \text{ \AA}$ [15]. The crystal structure of lithium iron phosphate was created using VESTA

[16] and the crystallographic data was taken from [17]. The crystallographic data used for creating the crystal structure is given in Figure 2.2: .

```
=====
Title                New structure

Lattice type         P
Space group name      P n m a
Space group number    62
Setting number        1

Lattice parameters

  a      b      c    alpha    beta    gamma
10.45300  6.08650  4.75340  90.0000  90.0000  90.0000

Unit-cell volume = 302.421693 Å^3

Structure parameters

      x      y      z    Occ.    B    Site    Sym.
1 Li  XX      0.00000  0.00000  0.00000  1.000  1.000  4a    -1
2 Fe  XX      0.21851  0.25000  0.52397  1.000  1.000  4c     .m.
3 P   XX      0.40533  0.25000  0.08116  1.000  1.000  4c     .m.
4 O   XX      0.33431  0.04709  0.21386  1.000  1.000  8d     1
5 O   XX      0.04271  0.25000  0.29341  1.000  1.000  4c     .m.
6 O   XX      0.40348  0.25000  0.75768  1.000  1.000  4c     .m.
=====

Number of polygons and unique vertices on isosurface = 0 (0)
841 atoms, 960 bonds, 192 polyhedra; CPU time = 11 ms
```

Figure 2.2: Summary of data used for creating Crystal structure of Lithium iron phosphate in VESTA.

Figure 2.3: The crystal structure of Lithium iron phosphate.

The crystal structure of lithium iron phosphate with 24-unit cells is shown in Figure 2.3: . The black lines at the lower left corner show one-unit cell. Li is shown in red. The iron atom and 6 oxygen atoms form an octahedral coordination sphere, described as $FePO_6$, with the Fe ion at the center. The phosphate groups, PO_4 , are tetrahedral. The octahedral are shown in yellow and tetrahedral in red (Figure 2.3:).

2.2.1.2 Two phase structure of Lithium Iron Phosphate

$LiFePO_4$ exhibits a two-phase system with a single lithium poor phase called heterosite ($FePO_4$) and lithium rich phase called triphylite ($LiFePO_4$).

$$Li_xFePO_4 \equiv xLiFePO_4 + (1-x)FePO_4$$

Both phases are olivine type orthorhombic structures with the P_{nma} space group although the lattice constants for both the phases differ and contribute to $\sim 7\%$ volumetric contraction from triphylite when heterosite is formed. The lattice constants for FePO_4 and LiFePO_4 are shown in Table 2.1: . The phase boundary between FePO_4 and LiFePO_4 is coherent which forms when two crystals match perfectly at the interface plane.

Table 2.1: Lattice constants of triphylite and heterosite [18].

Phase	Triphylite (LiFePO_4)	Heterosite (FePO_4)
a (Å)	10.329	9.814
b (Å)	6.007	5.789
c (Å)	4.691	4.782
Volume (Å ³)	291.1	271.7

The phase diagram of Li_xFePO_4 is constructed using XRD by [19] and is shown in Figure 2.4: . The main features of the phase diagram include a stable two single phase system ($\text{FePO}_4 + \text{LiFePO}_4$) below a temperature of 200°C . Thus, the two phases α and β coexist when the temperature is below 200°C . A distorted solid solution phase starts to evolve when the temperature is increased beyond 200°C . The lithium ions are distributed uniformly in the crystal structure of distorted solid solution phase. The α and β phases disappear and only the distorted phase exists at temperature above 300°C . The eutectoid point where a solid solution changes to two solid solutions (α and β phases) appear at $x=0.6$ at a temperature of around 200°C . The existence of a two-phase system at lower temperature is attributed to the lower Gibbs energy associated with the configuration with respect to a single homogeneous Li_xFePO_4 system.

Figure 2.4: Phase diagram of Li_xFePO_4 [19].

2.2.2 NMC

Lithium Nickel Manganese Cobalt Oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) commonly known as NMC is another high capacity cathode used in electric vehicle applications. It is formed by replacement of Co in LiCoO_2 by Mn and Ni. Thus, the electrochemical stability, cycle rate and capacity can be tuned by varying the composition of Ni, Mn and Co. NMC belongs to the class of materials having $\alpha\text{-NaFeO}_2$ (R3m) structure where alternate layers are occupied by Li, O and transition metals (TMs). The O atoms form an octahedron with TM elements positioned at centres of the octahedrons. The crystal structure of NMC (Lithium Nickel Manganese Oxide) was created using VESTA [16] and

the crystallographic data was taken from [20]. The crystallographic data used for creating the crystal structure is given in Figure 2.5:

```
=====
Title           New structure

Lattice type     R
Space group name R -3 m
Space group number 166
Setting number   1

Lattice parameters

  a      b      c    alpha    beta    gamma
2.89600  2.89600 14.25900 90.0000 90.0000 120.0000

Unit-cell volume = 103.565900 Å^3

Structure parameters

      x      y      z    Occ.    B    Site    Sym.
1 Li  XX    0.00000  0.00000  0.00000  1.000  1.000  3a    -3m
2 M   XX    0.00000  0.00000  0.50000  1.000  1.000  3b    -3m
3 O   XX    0.00000  0.00000  0.25610  1.000  1.000  6c     3m
=====

Number of polygons and unique vertices on isosurface = 0 (0)
172 atoms, 180 bonds, 30 polyhedra; CPU time = 152 ms
```

Figure 2.5: Summary of data used for creating Crystal structure of NMC in VESTA.

Figure 2.6: The crystal structure of NMC.

The crystal structure of NMC is shown in Figure 2.6: . The black lines show unit cell. Li is shown in green, oxygen in red and TM in purple inside the octahedrons.

2.3 Electrochemical Characterization: Cyclic Voltammetry

Electrochemistry is the branch of chemistry that deals with the relations between electrical and chemical phenomena and has been used as a powerful tool to probe chemical reactions involving electron transfers. In electrochemistry, it is essential to understand the electron transfer between electrode surface and the analyte in solution. Nernst Equation relates the potential of an

electrochemical cell (E) to the standard potential of a species (E^0) and the relative activities of the oxidized (Ox) and reduced (Red) analyte in the system at equilibrium. The Nernst Equation (Equation 2-4) is given below where R is the universal gas constant, n is the number of electrons, F is the Faraday's constant and T is the temperature.

$$E = E^0 + \frac{RT}{nF} \ln \frac{Ox}{Red} \quad 2-4$$

Cyclic Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode and measuring the resulting current. Figure 2.7: shows the relationship between time and applied potential for a generic cyclic voltammetry experiment. The potential is first scanned negatively (cathodic trace) in the forward scan from the starting potential E_1 to the switching potential E_2 . The scan direction is then reversed, and the potential is scanned positively from E_2 to E_1 known as the anodic trace. The Potential E_2 is called the switching potential.

Figure 2.7: Generic Cyclic Voltammogram excitation signal.

The Cyclic Voltammogram corresponding to the excitation signal of Figure 2.7: for the reaction between (ferrocenium) Fc^+ and (ferrocene) Fc is shown in Figure 2.8. The shape of the curve is based on the movement of species to and from the electrode and bulk diffusion.

Figure 2.8: Cyclic Voltammogram for a generic excitation signal.

When the potential is scanned negatively (cathodically) from point A to point D (Figure 2.8), Fc^+ is reduced to Fc and its concentration is depleted near the surface. The current is dictated by the delivery of additional Fc^+ via diffusion from the bulk solution at point C, where the peak cathodic current ($i_{p,c}$) is observed. The volume of solution at the surface of the electrode containing the

reduced Fc, called the diffusion layer, continues to grow throughout the scan. This slows down the mass transport of Fc^+ to the electrode. Thus, upon scanning to more negative potentials, the rate of diffusion of Fc^+ from the bulk solution to the electrode surface becomes slower, resulting in a decrease in the current as the scan continues ($\text{C} \rightarrow \text{D}$). The scan direction is reversed as the switching potential (D) is reached, and the potential is scanned in the positive (anodic) direction. While the concentration of Fc^+ at the electrode surface was depleted, the concentration of Fc at the electrode surface increased, satisfying the Nernst equation. The Fc present at the electrode surface is oxidized back to Fc^+ as the applied potential becomes more positive. At points B and E, the concentrations of Fc^+ and Fc at the electrode surface are equal, following the Nernst equation, $E = E_{1/2}$. The two peaks are separated due to the diffusion of the analyte to and from the electrode. Two conventions commonly used to report CV data are the US and IUPAC convention. The sign conventions are shown in Figure 2.9. The arrow indicates the beginning and sweep direction of first scan (forward scan).

Figure 2.9: Sign Convention for Cyclic Voltammetry [21].

2.4 Dislocations and Burgers Vector

Dislocations play a significant role in materials and have served mankind since it first started using metals. Plastic deformation of metals due to dislocations has helped man in bronze age and iron age to grow rapidly. It is because of dislocations that plasticity can be achieved even in non-metallic crystalline materials. Therefore, it becomes important to study the effect of dislocations in energy materials in today's era where Li-ion batteries are of great importance in day to day applications. As the periodic structure of atoms in a material was established using x-ray making it a perfect crystal, defects were soon discovered in the materials with a simple idea of nothing is perfect. Defects were then classified into point defects (vacancies and interstitials), line defects (edge dislocation and screw dislocation) and planar defects which included stacking faults and grain boundaries. Although each defect changes the material properties in its unique way, our study is focused on dislocations that occur in cathode material lithium iron phosphate by the mechanism explained by Huang and Wang [12]. Dislocations are linear crystallographic defects around which

the atoms of crystal lattice are misaligned. The two main types of dislocations include edge dislocation and screw dislocations. Dislocations having characters of both edge and screw dislocations are also common and are called mixed dislocations.

2.4.1 Edge Dislocation

An edge dislocation is an extra plane of atoms in a crystal. It is a linear defect as the locus of the defective points produced in the lattice in the crystal is along a line as shown in Figure 2.10: . Due to an extra plane of atoms added, the interatomic bonds are significantly distorted in immediate vicinity of the dislocation.

Figure 2.10: Edge Dislocation in a Cubic Crystal.

Since dislocations help in plastic deformation of a material at a much lower stress than in a perfect crystal, it is important to know the mechanism behind it. The dislocation motion during plastic

deformation is analogous to the movement of a caterpillar. Like a caterpillar which creates a hump in its body and moves forward by moving the hump forward by a small amount. This way a caterpillar avoids exerting a large force at once to move its entire body. As shown in Figure 2.11: , the dislocation moves similarly a small amount at a time by slipping one plane at a time to the right. Thus, the dislocation propagates through the entire crystal and causes deformation by moving one plane at a time. As only a small number of interatomic bonds are broken from moving one plane at a time, the shear force required to cause deformation is less than in a perfect crystal.

Figure 2.11: Representation of Analogy between Caterpillar and dislocation movement.

2.4.2 Screw Dislocation

A screw dislocation derives its name from the helical or spiral path that is traced around the dislocation by the plane of atoms. A screw dislocation is produced when a perfect crystal is cut along a plane partially and then atoms on one side are shifted parallel to the cut surface through one atom spacing corresponding to the atoms on the other side. This shift is parallel along the

dislocation line. A screw dislocation is shown in Figure 2.12: in which upper front region of the lattice is shifted one atomic distance right relative to the bottom portion.

Figure 2.12: A screw dislocation.

2.4.3 Burgers Vector

A Burgers vector represents the magnitude and direction of the lattice distortion associated with a dislocation in a lattice. A Burgers vector is represented by $\mathbf{b}$. The Burgers vector for a dislocation is calculated starting from a perfect lattice. A rectangle is drawn with sides equal to integer multiples of unit edge length around the site where dislocation is to be introduced. Then the dislocation in the crystal is introduced which distorts and changes both the geometry of the lattice and the drawn rectangle. The rectangle now turns into an open geometric figure. The vector required to close this distorted open geometric figure is the Burgers vector. The Burgers vector is from start to finish of the geometric open figure if the rectangle was drawn initially in a clockwise manner and vice-versa. Figure 2.13: shows the determination of the Burgers vector in an edge and a screw dislocation.

(a)

(b)

Figure 2.13: Determination of Burgers Vector in (a) Edge Dislocation (b) Screw Dislocation.

The Burgers vector is specified by miller indices (***h k l***). The magnitude of a Burgers vector in BCC and FCC lattice is given by:

$$\|\mathbf{b}\| = (a/2)\sqrt{h^2 + k^2 + l^2},$$

where *a* is the unit edge length. The magnitude of Burgers vector in a simple cubic lattice is given by

$$\|\mathbf{b}\| = a\sqrt{h^2 + k^2 + l^2}.$$

The Burgers vector of an edge dislocation is perpendicular to the dislocation line whereas the Burgers vector of a screw dislocation is in parallel to the dislocation line.

2.5 Stresses associated with Dislocations

As edge dislocations are introduced in material corresponding to an extra plane or a missing plane of atoms from the lattice, stresses associated with dislocations are also generated within the crystal. The region of edge dislocation with an extra half plane experiences state of compression and the region of edge dislocation without an extra plane experiences tension. An edge dislocation with an extra half plane is shown in Figure 2.14: where atoms in upper half region with extra half plane introduced between them experiences compressive forces and atoms in lower half region experiences tensile forces.

Figure 2.14: Nature of stresses in edge dislocation.

The classical analytical solution for stress field of an edge dislocation assuming isotropic properties of material is given below [22]:

$$\sigma_{xx} = -D \cdot y \frac{3x^2 + y^2}{(x^2 + y^2)^2} \quad 2-5$$

$$\sigma_{yy} = D \cdot y \frac{x^2 - y^2}{(x^2 + y^2)^2} \quad 2-6$$

$$\sigma_{xy} = \sigma_{yx} = D \cdot x \frac{x^2 - y^2}{(x^2 + y^2)^2} \quad 2-7$$

$$\sigma_{zz} = \nu \cdot (\sigma_{xx} + \sigma_{yy}) \quad 2-8$$

$$\sigma_{zx} = \sigma_{yz} = \sigma_{zy} = 0, \quad 2-9$$

where $D = Gb / 2\pi(1-\nu)$. This classical analytical solution is based on linear elastic theory assuming isotropic properties of materials. The atoms in the core region of dislocation experiences large strain equal to about a lattice constant where linear theory of elasticity does not hold and the analytical solution fails to calculate stresses. However, most cathode materials have anisotropic properties. The cathode material lithium iron phosphate in study has orthorhombic crystal structure and anisotropic elastic constants as given in [23]. Thus a more general analytical solution of dislocations using anisotropic property was given by V.L. Indenbom and J. Lothe [24]. The solution holds good for orthorhombic materials such as lithium iron phosphate where anisotropic

properties cannot be ignored, and elastic constants vary in different directions. The solution for stress fields of a dislocation with arbitrary Burgers vector is given by Equation 2-10.

$$\sigma_{ij} = \frac{b_x \lambda (C_{12} - \bar{C}_{11})}{4\pi q^2 t^2 \bar{C}_{11} C_{66} \sin \phi} \left\{ \begin{aligned} & C_{ij11} \left[(\bar{C}_{11} + C_{12} + C_{12}) x^2 y + \lambda^2 C_{66} y^3 \right] - C_{ij12} (\bar{C}_{11} + C_{12}) (x^3 - \lambda^2 x y^2) \\ & - \frac{C_{ij22}}{C_{22}} \left[(\bar{C}_{11} C_{12} + C_{12}^2 + 2C_{12} C_{66} + \bar{C}_{11} C_{66}) x^2 y - \bar{C}_{11} C_{66} \lambda^2 y^3 \right] \end{aligned} \right\}$$

$$- \frac{b_y \lambda (C_{12} - \bar{C}_{11})}{4\pi q^2 t^2 \bar{C}_{11} C_{66} \sin \phi} \left\{ \begin{aligned} & C_{ij22} \left[(\bar{C}_{11} + C_{12} + C_{66}) \lambda^2 x y^2 + C_{66} x^3 \right] - C_{ij12} (\bar{C}_{11} + C_{12}) (\lambda^2 y^3 - x^2 y) \\ & - \frac{C_{ij11}}{C_{11}} \left[(\bar{C}_{11} C_{12} + C_{12}^2 + 2C_{12} C_{66} + \bar{C}_{11} C_{66}) \lambda^2 x y^2 - \bar{C}_{11} C_{66} x^3 \right] \end{aligned} \right\} \quad 2-10$$

where

$$\bar{C}_{ij} = (C_{11} C_{22})^{1/2}, \lambda = (C_{11} / C_{22})^{1/4}, \phi = \frac{1}{2} \cos^{-1} \left(\frac{C_{12}^2 + 2C_{12} C_{66} - \bar{C}_{11}^2}{2\bar{C}_{11} C_{66}} \right), q^2 = x^2 + 2xy\lambda \cos \phi + y^2 \lambda^2$$

and $t^2 = x^2 - 2xy\lambda \cos \phi + y^2 \lambda^2$

The solution for stress field of a screw dislocation on ab-plane as given by [24] is given by Equation 2-11 and Equation 2-12.

$$\sigma_{xz} = \frac{b_z}{2\pi} (C_{44} C_{55} - C_{45}^2)^{1/2} \left(\frac{C_{45} x - C_{55} y}{C_{44} x^2 - 2C_{45} xy + C_{55} y^2} \right) \quad 2-11$$

$$\sigma_{yz} = \frac{-b_z}{2\pi} (C_{44} C_{55} - C_{45}^2)^{1/2} \left(\frac{C_{44} x - C_{45} y}{C_{44} x^2 - 2C_{45} xy + C_{55} y^2} \right) \quad 2-12$$

The solution described above for orthorhombic material using anisotropic material is used for lithium iron phosphate to calculate the stress field around two dislocations of different orientations using superimposition during phase transformation.

2.6 Dislocations associated with Lithium Iron Phosphate

It has been suggested that due to layered structure of lithium iron phosphate, Li ions travel in and out of tunnels along the b direction [25]. During repetitive and fast deintercalation/intercalation during charging/discharging, one or few more layers of lithium might be filled partially or skipped entirely causing dislocations of edge and screw characters as suggested by [12]. Edge dislocations thus formed in lithium iron phosphate can have different Burgers vector depending on how the lithium was filled. An edge dislocation with Burgers vector is shown in Figure 2.15: and is formed when a layer is only partially filled during intercalation with (100) extra half plane and a (010) glide plane.

Figure 2.15: Edge dislocation with $b_x=1$, $b_y=0$ in Lithium iron phosphate lattice (a) Isometric view (b) Top view.

An edge dislocation as shown in Figure 2.16: is created when Li ions in the crystal are filled non-homogeneously during fast intercalation and deintercalation during discharging/charging. Thus, Li ions at one end become higher in number than at another end. The glide plane of the dislocation thus becomes (100) along with extra half plane as (100) .

Figure 2.16: Edge dislocation with $b_x=0$, $b_y=-0.6$ in Lithium iron phosphate lattice (a) Isometric view (b) Top view.

CHAPTER 3: STRESS FIELD AROUND DISLOCATIONS DURING PHASE TRANSFORMATION AND CYCLIC VOLTAMMETRY

3.1 Stresses during phase transformation

The stresses around dislocations depend on the elasticity of the material being considered. The lithium rich and lithium poor phase formed during phase transformation of lithium iron phosphate have different material properties and thus have different elasticity. During phase transformation of lithium iron phosphate, the elasticity changes between that of LiFePO_4 and FePO_4 and thus the stresses around dislocations have values intermediate between that of LiFePO_4 and FePO_4 . For our study, the change in elasticity of the material during phase transformation was taken into account by the amount of phase transformation that occurred in the material at any instant during electrochemical reaction. Elastic constants of the electrode material change as the lithium iron phosphate progressively undergoes phase transformation. The change in elastic constant at any instant of phase transformation is given by Equation 3-1.

$$[C_{ij}] = (1-x)[C_{ij}]_{\text{FeO}_4} + x[C_{ij}]_{\text{LiFeO}_4} \quad 3-1$$

where x is the amount of phase transformation and varies from 0 to 1 during phase transformation. The x equal to 0 indicates that no phase transformation has taken place in material whereas x equal to 1 indicates that all of the LiFePO_4 has changed to FePO_4 and corresponds to 100% phase transformation. The elastic constants for LiFePO_4 and FePO_4 are taken from [23] and given in Table 3.1:.

Table 3.1: Material Properties used in the calculation of stress fields in dislocations in lithium iron phosphate during phase transformation [23].

FePO ₄		LiFePO ₄	
C ₁₁	137.4 GPa	C ₁₁	164.3 GPa
C ₂₂	146.0 GPa	C ₂₂	162.9 GPa
C ₃₃	132.0 GPa	C ₃₃	181.1 GPa
C ₄₄	40.8 GPa	C ₄₄	40.8 GPa
C ₅₅	38.2 GPa	C ₅₅	40.5 GPa
C ₆₆	42.1 GPa	C ₆₆	43.9 GPa
C ₁₂	41.0 GPa	C ₁₂	61.1 GPa
C ₁₃	29.1 GPa	C ₁₃	54.9 GPa
C ₂₃	29.1 GPa	C ₂₃	67.7 GPa

The stresses at any instant of time during phase transformation is calculated by Equation 2-10 by utilizing in the values of elastic constant obtained from Equation 3-1 using the values provided in Table 3.1:. Since there exists multiple dislocations simultaneously in any material, we have incorporated two dislocations in our model. Thus, the stresses inside lithium iron phosphate due to the occurrence of two simultaneous dislocations with arbitrary Burgers vector are calculated by the superposition principle. The stress at any point in material is equal to the sum of the stresses caused by an individual dislocation at that point considering the existence of that dislocation only in the material. Since multiple dislocations exist simultaneously in a material, we could incorporate many dislocations corresponding to a real-world material. But we chose 2 dislocations only to keep our model simple with less computational time. Also, two dislocations give a better visual

understanding of how the stress field changes during phase transformation as seen in the results shown later.

The model dimensions for lithium iron phosphate with lattice constants of lithium iron phosphate as given in Table 2.1: are $100L \times 60L$ with 60 unit cells of lithium iron phosphate where $L=10 \text{ \AA}$. An actual lithium iron phosphate particle is reported to be several hundred nanometres [26] and thus can be represented conveniently by our model. Also the model size is big enough to avoid dislocation cores of $4L \times 4L$ [27] where linear elastic theory fails. The model size of $100L \times 60L$ also depicts the overall stress distribution without any boundary effects. Mathematica [28] was used to numerically calculate the stresses given by Equation 2-10 and obtaining the stress values and distributions. The four components of stresses were numerically calculated for two dislocations during phase transformation of lithium iron phosphate. The two dislocations were fixed in their locations but differed in their orientation with respect to each other. The first dislocation was located at $(x,y)=(20L, -12L)$ whereas the second dislocation was located at $(x,y)=(40L, 24L)$ in the model. The orientation of one of the dislocation labelled Dislocation 2 was fixed with Burger vector $b_x=1$ and $b_y=0$ while the orientation of other dislocation labelled Dislocation 1 was varied by varying its Burgers vector.

Figure 3.1: shows the results of the stress evaluation of different stresses during phase transformation with dislocation 1 having Burgers vector $b_x=1, b_y=0$ and dislocation 2 with Burger vector $b_x=1, b_y=0$. Thus, both the dislocations have the same orientations by having the same Burgers vectors in this case. The amount of phase transformations tabulated against stresses in Figure 3.1: are chosen to correspond with $x=0.2, x=0.6$ and $x=0.9$. These values were chosen because they showed the maximum difference in stress fields during phase transformation and represent the phenomenon visually.

As shown in the Figure 3.1:, the stresses increase with increasing amount of phase transformation. Thus, as the phase transformation from LiFePO_4 to FePO_4 inside the lithium iron phosphate cathode start proceeding, cathode also start experiencing more dislocation-based stresses. The increase in the stresses will be proportional to the density of dislocations inside the material. It is also seen from Figure 3.1: that σ_{xx} shows the most variation during the phase transformation whereas σ_{yy} shows the least variation.

Figure 3.2: shows the results of the stress evaluation of different stresses during phase transformation with dislocation 1 having Burgers vector $b_x=1$, $b_y=0.6$ and dislocation 2 with Burger vector $b_x=1$, $b_y=0$. Thus, both the dislocations do not have the same orientation anymore in this case. The dislocation 2 was fixed in this orientation while the orientation of dislocation 1 was changed. As shown in the Figure 3.2: , the stresses in this case also increase with increasing amount of phase transformation. It is also seen from Figure 3.2: that all the stresses increase considerably during phase transformation as more and more LiFePO_4 is changed to FePO_4 compared to Figure 3.1: where σ_{xx} shows the most variation during the phase transformation and σ_{yy} shows the least variation and almost did not change.

Figure 3.1: Stress evaluation of different stresses during phase transformation.

Figure 3.3: shows the results of the stress evaluation of different stresses during phase transformation with dislocation 1 having Burgers vector $b_x=0, b_y=-0.6$ and dislocation 2 with Burger vector $b_x=1, b_y=0$. Compared to Figure 3.1: and Figure 3.2: , the stresses during phase transformation in Figure 3.3: does not increase as LiFePO_4 is progressively changed to FePO_4 . On the contrary, they decrease because of the particular orientation in which the two dislocations are oriented. Thus, it can be argued the increase or decrease in stresses around dislocations depends on the orientation of dislocations. Also comparing Figure 3.1: and Figure 3.2: , it was observed

that the change in stress in a particular direction is also dependent on orientation of dislocation.

Figure 3.1: showed that σ_{xx} , σ_{zz} and σ_{xy} changed significantly during the phase transformation whereas σ_{yy} almost did not change. However, the orientation of two dislocations in Figure 3.2: corresponded to significant changes in all components of stresses.

Figure 3.2: Stress evaluation of different stresses during phase transformation.

Figure 3.3: Stress evaluation of different stresses during phase transformation.

3.2 Phase transformation during Electrochemical Cycling

Electrode behaviour and diffusion of lithium in and out an electrode is probed by several electrochemical techniques. They provide insight into kinetics of phase transitions and are used to measure battery performance including amount of energy stored and the rate at which it is utilized. Cyclic Voltammetry (CV) is the most used electrochemical technique for characterization of electrode materials details of which are provided in section 2.3. The CV uses very small amount of material for experimentation and provides insight into the physical processes occurring in the

electrode. Thus, it is important to study how the stresses around dislocations during phase transformation changes the electrochemical reactions happening at electrodes. The Butler-Volmer Equation provides the most fundamental relationship between current and applied potential but lacks the effect of mechanical stresses inside the electrode. For this propose the effect of hydrostatic stress caused by dislocations was incorporated in the Butler-Volmer equation. The modified Butler-Volmer equation similar to [29] given by Equation 3-2 was then used to simulate cyclic voltammetry of lithium iron phosphate having dislocations.

$$i = i_0 \left\{ -\exp \left[(1 - \alpha) \frac{F(E - E_{eq}) - \sigma_h \Omega}{RT} \right] + \exp \left[-\alpha \frac{F(E - E_{eq}) - \sigma_h \Omega}{RT} \right] \right\} \quad 3-2$$

3.2.1 Derivation of the Modified Butler Volmer Equation

Figure 3.4: Variation of the free energy per mole lithium and the activation energy due to the applied electric potential and mechanical stresses [29].

Figure 3.4: shows the variation of the free energy per mole lithium and the activation energy due to the applied electric potential and mechanical stresses. Initially, the free energy for cathodic and anodic reactions are equal, and the electrode is in chemical equilibrium without any mechanical stresses.

$$\Delta G_{0c}^{\ddagger} = \Delta G_{0a}^{\ddagger} = \Delta G_0^{\ddagger} \quad 3-3$$

The chemical equilibrium is disturbed by the presence of mechanical stresses and applied electric overpotential. If the potential is changed by

$$\Delta E = E - E^{0'} \quad 3-4$$

Then the free energy of the oxidized state will be lowered relative to the reduced state by $F\Delta E$. For every mole of lithium intercalation the increase in the elastic energy is equal to the work done by the mechanical stress:

$$\Delta W_e = -\sigma_h \Omega \quad 3-5$$

This elastic energy increases the free energy of the reduced state by an amount equal to itself. Thus, the change in total free energy of the reduced state relative to the oxidized state is as follows:

$$F\Delta E + \Delta W_e \quad 3-6$$

This change in total free energy would contribute to the change in activation energies of cathodic and anodic reactions according to the charge transfer coefficients α and $(1-\alpha)$:

$$\Delta G_c^\ddagger = \Delta G_0^\ddagger + \alpha F\Delta E + \alpha \Delta W_e, \text{ and} \quad 3-7$$

$$\Delta G_a^\ddagger = \Delta G_0^\ddagger - (1-\alpha)F\Delta E - (1-\alpha)\Delta W_e \quad 3-8$$

Assuming the rate constants have an Arrhenius form [30] as follows:

$$k_f = A_f \exp(-\Delta G_c^\ddagger / RT), \quad 3-9$$

$$k_b = A_b \exp(-\Delta G_a^\ddagger / RT), \quad 3-10$$

$$k_f = A_f \exp(-\Delta G_{0c}^\ddagger / RT) \exp\left[-\alpha \frac{F(E - E^{0'}) - \sigma_h \Omega}{RT}\right], \text{ and} \quad 3-11$$

$$k_b = A_b \exp(-\Delta G_{0a}^\ddagger / RT) \exp[(1-\alpha) \frac{F(E - E^{0'}) - \sigma_h \Omega}{RT}] \quad 3-12$$

Considering there is no hydrostatic stress and the interface is in equilibrium with a solution in which

$$C_0^* = C_R^* \quad 3-13$$

$$E = E^{0'} \quad 3-14$$

This gives

$$k_f C_0^* = k_b C_R^* \implies k_f = k_b = k^0 \quad 3-15$$

Thus

$$k_b = k^0 \exp[(1-\alpha) \frac{F(E - E^{0'}) - \sigma_h \Omega}{RT}] \quad 3-16$$

Since the net current is given by:

$$i = i_c - i_a = nFA(k_f C_0(0,t) - k_b C_R(0,t)), \quad 3-17$$

the modified Butler Volmer equation thus becomes

$$i = i_0 \left\{ \frac{C_0(0,t)}{C_0^*} \exp[-\alpha \frac{F(E - E^{0'}) - \sigma_h \Omega}{RT}] - \frac{C_R(0,t)}{C_R^*} \exp[(1-\alpha) \frac{F(E - E^{0'}) - \sigma_h \Omega}{RT}] \right\} \quad 3-18$$

3.2.2 Relating Overpotential and Phase transformation

The over potential and phase transformation in storage electrodes was related by Lu et al. [29] with applications to nanoscale olivines. The paper serves as a base for the research in studying the

effect of mechanical stress in cyclic voltammetry. During CV, the applied over-potential may change the phase of the lithium iron phosphate which varies the hydrostatic stress around edge or screw dislocations in the particle. This change in hydrostatic stress changes the current as per the modified Butler Volmer Equation. A phase transition from crystalline LiFePO_4 to crystalline FePO_4 is thermodynamically favourable at $\Delta\phi$ (overpotential) > 0 . However, such transitions need to overcome energy barriers (or activation energies) and the probability of the thermally activated transition is proportional to $\exp(-\Delta F/kT)$. Figure 3.5: taken from Lu et al. [29] shows the variation of activation energy ΔF with increasing overpotential for transformation of a particle of $r=1\text{ }\mu\text{m}$ of crystalline LiFePO_4 (cLFP) to crystalline FePO_4 (cFP). The activation energy decreases with increasing overpotential and evolves toward zero at a critical overpotential $\Delta\phi_c = 30.283\text{ mV}$. Above this overpotential, the phase transformation is barrier less and occurs spontaneously.

Figure 3.5: Overpotential dependence of the activation energy, ΔF for transformation of a particle of $r=1\text{ }\mu\text{m}$ of crystalline LiFePO_4 (cLFP) to crystalline FePO_4 (cFP) with increasing overpotential [31].

The activation energy, ΔF decreases almost linearly with increasing overpotential up to the point where it becomes zero. Due to thermally activated transition being proportional to $\exp(-\Delta F/kT)$, the phase transformation of crystalline LiFePO_4 (cLFP) to crystalline FePO_4 (cFP) can be considered to be exponential. Thus, a sigmoid function was used in our model to show the variation of phase transformation from 0 to $\Delta\phi_c = 30.283$ mV. The variation of amount of phase transformation during cyclic voltammetry with an overpotential range of -3V to 3V is shown in Figure 3.6:.

Figure 3.6: Variation of amount of phase transformation with applied overvoltage during Cyclic Voltammetry.

3.3 Effect of Phase transformation on Cyclic Voltammogram

We have developed a relation between stresses and phase transformation in section 3.1 and between phase transformation and applied overvoltage in section 3.2. Now the effect of changing stress field around dislocations during phase transformation can be studied combining the knowledge of the two. The stresses field around dislocations were shown in Figure 3.1; Figure

3.2: and Figure 3.3: . The hydrostatic stress around dislocation was then calculated using Equation 3-19 at any instance of cyclic voltammetry corresponding to an amount of phase transformation happened at that instant.

$$\sigma_h = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} \quad 3-19$$

The hydrostatic stress thus calculated at any instance of cyclic voltammetry corresponding to a particular amount of phase transformation was then used in the modified Butler Volmer equation to simulate the cyclic voltammogram.

The CV curves obtained using the modified Butler Volmer equation are shown in Figure 8 for three different orientations of two dislocations. The region of phase transformation is shown in grey color inside the CV curve and it was seen that the stress changes inside the material during phase transformation due to which the CV curves for phase transformation and without phase transformation were different. A normal CV curve for an electrochemically reversible reaction without any stresses is also shown alongside with blue dotted lines for comparison. It can be concluded that the dislocations can be useful for changing the characteristics of CV curve and thus can be useful according to the desired overpotential use range of the battery. For example, we see that the current decreases for the same overpotential due to the stresses induced by dislocations for certain overpotential range (between anodic peak and zero overpotential for forward scan). The reverse effect of increasing current for same overvoltage can be created if the nature of stress (compressive or tensile) is changed by varying orientation of dislocations. Thus, low current or high current can be obtained for the same voltage in a CV curve depending on difference usages.

Figure 3.7: CV curve for 3 different orientations of two dislocations with partial molar volume of lithium iron phosphate taken as 0.0001 (a) Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$ (b) Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$ (c) Dislocation 1 with Burgers Vectors $b_x=0$, $b_y=-0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$.

Comparing the Figure 3.7: (a), (b) and (c), it is observed that the reduction in current for the same overpotential is more obvious in Figure 3.7: (a) than one shown in Figure 3.7: (b). This is attributed to the particular orientation of the dislocations corresponding to the cyclic voltammograms considered. In addition, comparing Figure 3.7: (a) and Figure 3.7: (c), the reduction in current is almost the same for a particular overpotential because both CV curves correspond to the dislocations having Burgers vectors along crystallographic directions (pure edge dislocations). Thus, three important observations are made from Figure 3.7::

1. The presence of dislocations changes the electrochemical performance of electrodes dramatically which were revealed by the shift of the shape of the CV curve, as shown by comparing the blue dotted curves and red dashed curves in Figure 3.7:. This change in shape is attributed to the presence of stresses around dislocations.
2. Phase transformation inside lithium iron phosphate electrode having dislocations causes further change in electrochemical performance of the electrode as seen by comparing red dashed curves and black solid curves in Figure 3.7:. As soon as the phase transformation starts inside the material due to applied overvoltage, the stress field around dislocations changes along with its electrochemical behavior. The more the phase transformation occurs by increasing overpotential, the current reduces more with respect to its value without having any phase transformation up to the anodic peak and then increases beyond the anodic peak. The reverse phenomenon happened for the cathodic peak.
3. The amount of increase or decrease in value of current at an applied overvoltage depends on the orientation of dislocations as seen in Figure 3.7:. The CV curves with dislocation oriented specifically along one axis have almost identical CV curves. Whereas the

dislocation orientation in which dislocation 1 has Burger vector ($b_x=1$, $b_y=0.6$) not aligned specifically along one axis has less change in current at particular overvoltage.

Thus, it can be concluded from Figure 3.7: that presence and orientation of two dislocations during phase transformation are the two primary factors that affect the electrochemical behaviour of the material during battery charge-discharge cycles.

Figure 3.8 shows the effect of increasing the scan rate of the forward and backward scan on the CV curve. It is seen that increasing the scan rate increases the current for the applied over-voltage for all the three different orientations of the dislocations studied. The dashed lines in shows the CV curves without phase transformation and solid lines shows CV curves with phase transformation corresponding to a particular scan rate. The key observations from the are:

1. The increase in current for a particular overvoltage is a phenomenon that is independent of the orientation of dislocations considered in our model.
2. The decrease in current corresponding to a particular overvoltage value before anodic peak and increase in current after the anodic peak is somehow proportional to the scan rate . Increase scan rates show increased deviation of current from a CV curve for material in which there is no phase transformation.

Figure 3.8 Effect of Scan rate on CV curve for three different orientations of two dislocations with Partial molar volume of lithium iron phosphate taken as 0.0001 (a) Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$ (b) Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$ (c) Dislocation 1 with Burgers Vectors $b_x=0$, $b_y=-0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$.

Scan rate along with orientation of dislocation in lithium iron phosphate can thus be used to change the electrochemical behaviour of lithium iron phosphate as per application requirements. If the application in which the battery is used encounters high over-voltages greater than at which anodic peak is observed, presence of dislocations increases the current for the same overpotential. The presence of dislocations inside material also helps if the application requires low overvoltage and low current. Thus it can be concluded that the combined effects of the stresses induced around dislocations during phase transformation and high scan rate can be used for creating batteries for specific applications based on the overvoltage encountered in those applications.

CHAPTER 4: CONCLUSION

4.1 Summary

The research deals with studying the effect of dislocation-based stresses during phase transformation of a lithium iron phosphate cathode on a cyclic voltammogram. A model consisting of two dislocations inside a lithium iron phosphate material was used to calculate stress fields using linear elastic theory and the superposition method. The stress fields around dislocations during phase transformation of LiFePO_4 to FePO_4 were then numerically simulated using Mathematica (Wolfram Research, Champaign, IL) incorporating the anisotropic properties of the material. The results showed that the stress inside material increase or decrease during phase transformation and does not remain constant. The variations in stress depends on the orientation of the dislocations. While in one case, some dislocations may be oriented in such a way that they increase the overall stress as opposed to the other case in which they are oriented to decrease the overall stress. Also, it was observed that the amount of increase of a particular component of stress during phase transformation was dependent on orientation of dislocations. While one orientation showed significant increase in all components of stress, the other orientation corresponded to significant increase only in some of the components with some remaining nearly constant throughout the phase transformation. A modified Butler Volmer equation was derived and used in simulating the reversible cyclic voltammogram of the lithium iron phosphate using MATLAB. The modified BV equation incorporated the effect of stress caused by dislocations during phase transformation. It was observed that the presence of dislocations changes the electrochemical behaviour of the electrode material by shifting the CV curves. This change in electrochemical behaviour is attributed to the presence of stresses around dislocations. The current reduced significantly with respect to its value without having any phase transformation up to the anodic

peak and then increased beyond the anodic peak. The reverse phenomenon also happened for the cathodic peak. The amount of changes in current at an applied overvoltage depended on the orientation of dislocations. The CV curves with dislocation oriented specifically along one axis had almost identical CV curves whereas the CV curves with dislocations not aligned specifically along one axis had less change in current at particular overvoltage. The effect of increasing scan rate was also studied on cyclic voltammogram for lithium iron phosphate. The increase in current at peaks was found independent of the orientation of dislocations considered. Also, the decrease in current corresponding to a particular overvoltage value before an anodic peak and increase in current after the anodic peak was found to be somehow proportional to the scan rate. Increased scan rates showed increased deviation of current from a CV curve for material in which there is no phase transformation. The results provided an insight into how presence of defects and phase transformation changes the electrochemical behaviour of the material. It was concluded that the combined effect of the stresses induced around dislocations during phase transformation and high scan rate can be used for creating batteries for specific applications based on the overvoltage encountered in those applications. Thus, defects inside battery electrodes can be engineered to change the electrochemical behaviour of the material, an example of which is the orientation and dislocation density considered in this thesis.

4.2 Future work

Intensive research has been done on lithium iron phosphate till date. Elastic properties of lithium iron phosphate are thus known and can be used to simulate electrochemical behaviour of the same. However, with increasing battery demand, newer and better materials are taking over the lithium iron phosphate as a choice for cathode. NMC is one such complementary potential material of

future battery applications. NMC is a newer material and much of research needs to be done to better understand its elastic properties and electrochemical performance completely. A similar model can be developed and used to understand the effect of dislocation-based stresses during phase transformation on electrochemical behaviour of NMC. Our model serves as a base model for the NMC model. Also, more than 2 dislocations can be considered in future work corresponding to high dislocation density in the material.

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APPENDICES

Appendix A: Mathematica Code for Calculating Stress Fields Around Dislocations of different orientations during Phase Transformation

1. Mathematica Code for calculating σ_{xx} during Phase Transformation

```

Eiso=10^9*(138.9^2+138.9*72.8-2*72.8^2)/(138.9+72.8)
viso=72.8/(138.9+72.8)
c11iso=(Eiso*(1-viso))/(1-viso-2*viso^2)
c12iso=(Eiso*viso)/(1-viso-2*viso^2)
c44iso=Eiso/(2+2viso)
uiso=33.05*10^9
(* Elastic Constants for Iron Phosphate *)
A11=137.4*10^9
A22=146*10^9
A33=132*10^9
A44=40.8*10^9
A55=38.2*10^9
A66=42.1*10^9
A12=41*10^9
A13=29.1*10^9
A23=29.1*10^9
(* Elastic Constants for Lithium Iron Phosphate*)
B11=164.3*10^9
B22=162.9*10^9
B33=181.1*10^9
B44=40.8*10^9
B55=40.5*10^9
B66=43.9*10^9
B12=61.1*10^9
B13=54.9*10^9
B23=67.7*10^9
(* Elastic Constants During phase transformation *)
c11=((1-conc)*A11)+(conc*B11)
c22=((1-conc)*A22)+(conc*B22)
c33=((1-conc)*A33)+(conc*B33)
c44=((1-conc)*A44)+(conc*B44)
c55=((1-conc)*A55)+(conc*B55)
c66=((1-conc)*A66)+(conc*B66)
c12=((1-conc)*A12)+(conc*B12)
c13=((1-conc)*A13)+(conc*B13)
c23=((1-conc)*A23)+(conc*B23)
cd11=Sqrt[c11*c22]
λ=Sqrt[Sqrt[c11/c22]]
φ=1/2*ArcCos[(c12*c12+2*c12*c66-cd11*cd11)/(2*cd11*c66)]
Q1[x_,y_]:= (x-m1)*(x-m1)+2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ

```

```

T1[x_,y_]:= (x-m1)*(x-m1)-2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
Q2[x_,y_]:= (x-m2)*(x-m2)+2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ
T2[x_,y_]:= (x-m2)*(x-m2)-2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ

```

```

(*Two Dislocations--Any Burgers vector direction & any location*)
(*Direction and Position Can be Changed for different Cases*)

```

```

m1=-20
n1=-12
m2=40
n2=24
b1x=1
b1y=0
b2x=1
b2y=0

```

```

(*Sigma xx Calculation For the Desired Orientation*)

```

```

σ11[x_,y_]:=((b1x*λ*(c12-
cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(c11*((cd11+c12+c66)*(x-m1)^2*(y-
n1)+λ*λ*c66*(y-n1)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m1)^2*(y-
n1)-cd11*c66*λ*λ*(y-n1)^3))+((
-b1y*λ*(c12-
cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(c12*((cd11+c12+c66)*λ*λ*(x-m1)*(y-
n1)^2+c66*(x-m1)^3)-(c11/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*λ*λ*(x-m1)*(y-
n1)^2-cd11*c66*(x-m1)^3))+((b2x*λ*(c12-
cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(c11*((cd11+c12+c66)*(x-m2)^2*(y-
n2)+λ*λ*c66*(y-n2)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m2)^2*(y-
n2)-cd11*c66*λ*λ*(y-n2)^3))+((
-b2y*λ*(c12-
cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(c12*((cd11+c12+c66)*λ*λ*(x-m2)*(y-
n2)^2+c66*(x-m2)^3)-(c11/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*λ*λ*(x-m2)*(y-
n2)^2-cd11*c66*(x-m2)^3))
TraditionalForm[σ11[x,y]];

```

```

(*Creating a Table of Sigmaxx*)

```

```

Sigmaxx=Table[ContourPlot[{σ11[x,y]}/.{conc->i},{x,-50,50},{y,-30,30},(*cotrol stress
range*)PlotRange->{Full,All,{-10000000000,10000000000}},ColorFunction-
>"Rainbow",AspectRatio->Automatic,Contours->20,ContourLabels->Automatic,ClippingStyle-
>None],{i,0,1,0.1}]

```

```

(*Adding Slider to Table*)

```

```

finalone=Table[Column[{Slider[Sliderindex,ImageMargins->{{25,0},{1,1}},ImageSize-
>"Small",Appearance->"Labeled"],Part[Sigmaxx,(Sliderindex+0.1)*10]}],{Sliderindex,0,1,0.1}]

```

```

(*Reversing Table for Gif*)

```

```

finaltwo=Reverse[finalone]
final=Join[finalone,finaltwo]

```

(*Creating GIF*)

Export["Sigmaxx.gif",final,ImageSize->1280]

2. Mathematica Code for calculating σ_{yy} during Phase Transformation

Eiso= $10^9 \cdot (138.9^2 + 138.9 \cdot 72.8 - 2 \cdot 72.8^2) / (138.9 + 72.8)$

viso= $72.8 / (138.9 + 72.8)$

c11iso= $(Eiso \cdot (1 - viso)) / (1 - viso - 2 \cdot viso^2)$

c12iso= $(Eiso \cdot viso) / (1 - viso - 2 \cdot viso^2)$

c44iso= $Eiso / (2 + 2 \cdot viso)$

uiso= $33.05 \cdot 10^9$

(* Elastic Constants for Iron Phosphate *)

A11= $137.4 \cdot 10^9$

A22= $146 \cdot 10^9$

A33= $132 \cdot 10^9$

A44= $40.8 \cdot 10^9$

A55= $38.2 \cdot 10^9$

A66= $42.1 \cdot 10^9$

A12= $41 \cdot 10^9$

A13= $29.1 \cdot 10^9$

A23= $29.1 \cdot 10^9$

(* Elastic Constants for Lithium Iron Phosphate*)

B11= $164.3 \cdot 10^9$

B22= $162.9 \cdot 10^9$

B33= $181.1 \cdot 10^9$

B44= $40.8 \cdot 10^9$

B55= $40.5 \cdot 10^9$

B66= $43.9 \cdot 10^9$

B12= $61.1 \cdot 10^9$

B13= $54.9 \cdot 10^9$

B23= $67.7 \cdot 10^9$

(* Elastic Constants During phase transformation *)

c11= $((1 - \text{conc}) \cdot A11) + (\text{conc} \cdot B11)$

c22= $((1 - \text{conc}) \cdot A22) + (\text{conc} \cdot B22)$

c33= $((1 - \text{conc}) \cdot A33) + (\text{conc} \cdot B33)$

c44= $((1 - \text{conc}) \cdot A44) + (\text{conc} \cdot B44)$

c55= $((1 - \text{conc}) \cdot A55) + (\text{conc} \cdot B55)$

c66= $((1 - \text{conc}) \cdot A66) + (\text{conc} \cdot B66)$

c12= $((1 - \text{conc}) \cdot A12) + (\text{conc} \cdot B12)$

c13= $((1 - \text{conc}) \cdot A13) + (\text{conc} \cdot B13)$

c23= $((1 - \text{conc}) \cdot A23) + (\text{conc} \cdot B23)$

cd11= $\text{Sqrt}[c11 \cdot c22]$

$\lambda = \text{Sqrt}[\text{Sqrt}[c11/c22]]$

$\phi = 1/2 \cdot \text{ArcCos}[(c12 \cdot c12 + 2 \cdot c12 \cdot c66 - cd11 \cdot cd11) / (2 \cdot cd11 \cdot c66)]$

Q1[x_,y_]:= $(x - m1) \cdot (x - m1) + 2 \cdot (x - m1) \cdot (y - n1) \cdot \lambda \cdot \text{Cos}[\phi] + (y - n1) \cdot (y - n1) \cdot \lambda \cdot \lambda$

```

T1[x_,y_]:= (x-m1)*(x-m1)-2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
Q2[x_,y_]:= (x-m2)*(x-m2)+2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ
T2[x_,y_]:= (x-m2)*(x-m2)-2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ

```

```

(*Two Dislocations--Any Burgers vector direction & any location*)
(*Direction and Position Can be Changed for different Cases*)

```

```

m1=-20
n1=-12
m2=40
n2=24
b1x=1
b1y=0
b2x=1
b2y=0

```

```

(*Sigma yy Calculation For the Desired Orientation*)

```

```

σ22[x_,y_]:=((b1x*λ*(c12-
cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(c12*((cd11+c12+c66)*(x-m1)^2*(y-
n1)+λ*λ*c66*(y-n1)^3)-(c22/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m1)^2*(y-
n1)-cd11*c66*λ*λ*(y-n1)^3))+((-b1y*λ*(c12-
cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(c22*((cd11+c12+c66)*λ*λ*(x-m1)*(y-
n1)^2+c66*(x-m1)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*λ*λ*(x-m1)*(y-
n1)^2-cd11*c66*(x-m1)^3))+((b2x*λ*(c12-
cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(c12*((cd11+c12+c66)*(x-m2)^2*(y-
n2)+λ*λ*c66*(y-n2)^3)-(c22/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m2)^2*(y-
n2)-cd11*c66*λ*λ*(y-n2)^3))+((-b2y*λ*(c12-
cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(c22*((cd11+c12+c66)*λ*λ*(x-m2)*(y-
n2)^2+c66*(x-m2)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*λ*λ*(x-m2)*(y-
n2)^2-cd11*c66*(x-m2)^3));
TraditionalForm[σ22[x,y]];

```

```

(*Creating a Table of Sigmayy*)

```

```

Sigmayy=Table[ContourPlot[{σ22[x,y]}/.{conc->i},{x,-50,50},{y,-30,30},(*cotrol stress
range*)PlotRange->{Full,All,{-10000000000,10000000000}},ColorFunction-
>"Rainbow",AspectRatio->Automatic,Contours->20,ContourLabels->Automatic,ClippingStyle-
>None],{i,0,1,0.1}]

```

```

(*Adding Slider to Table*)

```

```

finalone=Table[Column[{Slider[Sliderindex,ImageMargins->{{25,0},{1,1}},ImageSize-
>"Small",Appearance->"Labeled"],Part[Sigmayy,(Sliderindex+0.1)*10]}],{Sliderindex,0,1,0.1}]

```

```

(*Reversing Table for Gif*)

```

```

finaltwo=Reverse[finalone]
final=Join[finalone,finaltwo]

```

```

(*Creating GIF*)

```

```

Export["Sigmayy.gif",final,ImageSize->1280]

```


3. Mathematica Code for calculating σ_{zz} during Phase Transformation

```

Eiso=10^9*(138.9^2+138.9*72.8-2*72.8^2)/(138.9+72.8)
viso=72.8/(138.9+72.8)
c11iso=(Eiso*(1-viso))/(1-viso-2*viso^2)
c12iso=(Eiso*viso)/(1-viso-2*viso^2)
c44iso=Eiso/(2+2viso)
uiso=33.05*10^9
(* Elastic Constants for Iron Phosphate *)
A11=137.4*10^9
A22=146*10^9
A33=132*10^9
A44=40.8*10^9
A55=38.2*10^9
A66=42.1*10^9
A12=41*10^9
A13=29.1*10^9
A23=29.1*10^9
(* Elastic Constants for Lithium Iron Phosphate*)
B11=164.3*10^9
B22=162.9*10^9
B33=181.1*10^9
B44=40.8*10^9
B55=40.5*10^9
B66=43.9*10^9
B12=61.1*10^9
B13=54.9*10^9
B23=67.7*10^9
(* Elastic Constants During phase transformation *)
c11=((1-conc)*A11)+(conc*B11)
c22=((1-conc)*A22)+(conc*B22)
c33=((1-conc)*A33)+(conc*B33)
c44=((1-conc)*A44)+(conc*B44)
c55=((1-conc)*A55)+(conc*B55)
c66=((1-conc)*A66)+(conc*B66)
c12=((1-conc)*A12)+(conc*B12)
c13=((1-conc)*A13)+(conc*B13)
c23=((1-conc)*A23)+(conc*B23)
cd11=Sqrt[c11*c22]
λ=Sqrt[Sqrt[c11/c22]]
φ=1/2*ArcCos[(c12*c12+2*c12*c66-cd11*cd11)/(2*cd11*c66)]
Q1[x_,y_]:= (x-m1)*(x-m1)+2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
T1[x_,y_]:= (x-m1)*(x-m1)-2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
Q2[x_,y_]:= (x-m2)*(x-m2)+2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ

```

$$T2[x_y_]:=(x-m2)*(x-m2)-2*(x-m2)*(y-n2)*\lambda*\cos[\phi]+(y-n2)*(y-n2)*\lambda*\lambda$$

(*Two Dislocations--Any Burgers vector direction & any location*)

(*Direction and Position Can be Changed for different Cases*)

$$m1=-20$$

$$n1=-12$$

$$m2=40$$

$$n2=24$$

$$b1x=1$$

$$b1y=0$$

$$b2x=1$$

$$b2y=0$$

(*Sigma zz Calculation For the Desired Orientation*)

$$\begin{aligned} \sigma11[x_y_]:= & ((b1x*\lambda*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*\sin[\phi]))*(c11*((cd11+c12+c66)*(x-m1)^2*(y-n1) \\ & +\lambda*\lambda*c66*(y-n1)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m1)^2*(y-n1) \\ & -cd11*c66*\lambda*\lambda*(y-n1)^3))+((-b1y*\lambda*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*\sin[\phi]))*(c12*((cd11+c12+c66)*\lambda*\lambda*(x-m1)*(y-n1)^2 \\ & +c66*(x-m1)^3)-(c11/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*\lambda*\lambda*(x-m1)*(y-n1)^2-cd11*c66*(x-m1)^3))+((b2x*\lambda*(c12-cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*\sin[\phi]))*(c11*((cd11+c12+c66)*(x-m2)^2*(y-n2) \\ & +\lambda*\lambda*c66*(y-n2)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m2)^2*(y-n2)-cd11*c66*\lambda*\lambda*(y-n2)^3))+((-b2y*\lambda*(c12-cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*\sin[\phi]))*(c12*((cd11+c12+c66)*\lambda*\lambda*(x-m2)*(y-n2)^2 \\ & +c66*(x-m2)^3)-(c11/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*\lambda*\lambda*(x-m2)*(y-n2)^2-cd11*c66*(x-m2)^3)) \end{aligned}$$

$$\begin{aligned} \sigma22[x_y_]:= & ((b1x*\lambda*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*\sin[\phi]))*(c12*((cd11+c12+c66)*(x-m1)^2*(y-n1) \\ & +\lambda*\lambda*c66*(y-n1)^3)-(c22/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m1)^2*(y-n1)-cd11*c66*\lambda*\lambda*(y-n1)^3))+((-b1y*\lambda*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*\sin[\phi]))*(c22*((cd11+c12+c66)*\lambda*\lambda*(x-m1)*(y-n1)^2 \\ & +c66*(x-m1)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*\lambda*\lambda*(x-m1)*(y-n1)^2-cd11*c66*(x-m1)^3))+((b2x*\lambda*(c12-cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*\sin[\phi]))*(c12*((cd11+c12+c66)*(x-m2)^2*(y-n2) \\ & +\lambda*\lambda*c66*(y-n2)^3)-(c22/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*(x-m2)^2*(y-n2)-cd11*c66*\lambda*\lambda*(y-n2)^3))+((-b2y*\lambda*(c12-cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*\sin[\phi]))*(c22*((cd11+c12+c66)*\lambda*\lambda*(x-m2)*(y-n2)^2 \\ & +c66*(x-m2)^3)-(c12/c22)*((c12*c12+cd11*c12+2*c12*c66+cd11*c66)*\lambda*\lambda*(x-m2)*(y-n2)^2-cd11*c66*(x-m2)^3)); \\ \sigma33[x_y_]:= & 0.34*(\sigma11[x,y]+\sigma22[x,y]); \end{aligned}$$

(*Creating a Table of Sigmazz*)

```
Sigmazz=Table[ContourPlot[{ $\sigma_{33}$ [x,y]}/.{conc->i},{x,-50,50},{y,-30,30},(*cotrol stress
range*)PlotRange->{Full,All,{ -10000000000,10000000000 }},ColorFunction-
>"Rainbow",AspectRatio->Automatic,Contours->20,ContourLabels->Automatic,ClippingStyle-
>None],{i,0,1,0.1}]
```

```
(*Adding Slider to Table*)
```

```
finalone=Table[Column[{Slider[Sliderindex,ImageMargins->{{25,0},{1,1}},ImageSize-
>"Small",Appearance->"Labeled"],Part[Sigmazz,(Sliderindex+0.1)*10]}],{Sliderindex,0,1,0.1}]
```

```
(*Reversing Table for Gif*)
```

```
finaltwo=Reverse[finalone]
```

```
final=Join[finalone,finaltwo]
```

```
(*Creating GIF*)
```

```
Export["Sigmazz.gif",final,ImageSize->1280]
```

4. Mathematica Code for calculating σ_{xy} during Phase Transformation

```
Eiso=10^9*(138.9^2+138.9*72.8-2*72.8^2)/(138.9+72.8)
```

```
viso=72.8/(138.9+72.8)
```

```
c1liso=(Eiso*(1-viso))/(1-viso-2*viso^2)
```

```
c12iso=(Eiso*viso)/(1-viso-2*viso^2)
```

```
c44iso=Eiso/(2+2viso)
```

```
uiso=33.05*10^9
```

```
(* Elastic Constants for Iron Phosphate *)
```

```
A11=137.4*10^9
```

```
A22=146*10^9
```

```
A33=132*10^9
```

```
A44=40.8*10^9
```

```
A55=38.2*10^9
```

```
A66=42.1*10^9
```

```
A12=41*10^9
```

```
A13=29.1*10^9
```

```
A23=29.1*10^9
```

```
(* Elastic Constants for Lithium Iron Phosphate*)
```

```
B11=164.3*10^9
```

```
B22=162.9*10^9
```

```
B33=181.1*10^9
```

```
B44=40.8*10^9
```

```
B55=40.5*10^9
```

```
B66=43.9*10^9
```

```
B12=61.1*10^9
```

```
B13=54.9*10^9
```

```
B23=67.7*10^9
```

```
(* Elastic Constants During phase transformation *)
```

```

c11=((1-conc)*A11)+(conc*B11)
c22=((1-conc)*A22)+(conc*B22)
c33=((1-conc)*A33)+(conc*B33)
c44=((1-conc)*A44)+(conc*B44)
c55=((1-conc)*A55)+(conc*B55)
c66=((1-conc)*A66)+(conc*B66)
c12=((1-conc)*A12)+(conc*B12)
c13=((1-conc)*A13)+(conc*B13)
c23=((1-conc)*A23)+(conc*B23)
cd11=Sqrt[c11*c22]
λ=Sqrt[Sqrt[c11/c22]]
φ=1/2*ArcCos[(c12*c12+2*c12*c66-cd11*cd11)/(2*cd11*c66)]
Q1[x_,y_]:= (x-m1)*(x-m1)+2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
T1[x_,y_]:= (x-m1)*(x-m1)-2*(x-m1)*(y-n1)*λ*Cos[φ]+(y-n1)*(y-n1)*λ*λ
Q2[x_,y_]:= (x-m2)*(x-m2)+2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ
T2[x_,y_]:= (x-m2)*(x-m2)-2*(x-m2)*(y-n2)*λ*Cos[φ]+(y-n2)*(y-n2)*λ*λ

```

(*Two Dislocations--Any Burgers vector direction & any location*)

(*Direction and Position Can be Changed for different Cases*)

```

m1=-20
n1=-12
m2=40
n2=24
b1x=1
b1y=0
b2x=1
b2y=0

```

(*Sigma xy Calculation For the Desired Orientation*)

```

σ12[x_,y_]:= ((b1x*λ*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(-
c66*(c12+cd11)*((x-m1)^3-λ*λ*(x-m1)*(y-n1)^2))+((
-b1y*λ*(c12-cd11))/(4*Pi*Q1[x,y]*T1[x,y]*cd11*c66*Sin[φ]))*(-
c66*(c12+cd11)*(λ*λ*(y-n1)^3-(x-m1)^2*(y-n1)))+(b2x*λ*(c12-
cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(-c66*(c12+cd11)*((x-m2)^3-λ*λ*(x-
m2)*(y-n2)^2))+((
-b2y*λ*(c12-cd11))/(4*Pi*Q2[x,y]*T2[x,y]*cd11*c66*Sin[φ]))*(-
c66*(c12+cd11)*(λ*λ*(y-n2)^3-(x-m2)^2*(y-n2)));

```

(*Creating a Table of Sigmaxy*)

```

Sigmaxy=Table[ContourPlot[{σ12[x,y]}/.{conc->i},{x,-50,50},{y,-30,30},(*cotrol stress
range*)PlotRange->{Full,All,{ -10000000000,10000000000 }},ColorFunction-
>"Rainbow",AspectRatio->Automatic,Contours->20,ContourLabels->Automatic,ClippingStyle-
>None],{i,0,1,0.1}]

```

(*Adding Slider to Table*)

```

finalone=Table[Column[{Slider[Sliderindex,ImageMargins->{{25,0},{1,1}},ImageSize-
>"Small",Appearance->"Labeled"],Part[Sigmaxy,(Sliderindex+0.1)*10]}],{Sliderindex,0,1,0.1}]

```

(*Reversing Table for Gif*)
 finaltwo=Reverse[finalone]
 final=Join[finalone,finaltwo]

(*Creating GIF*)
 Export["Sigmaxy.gif",final,ImageSize->1280]

Table A. 1: Average value of Different Stresses around dislocations with varying amount of Phase Transformation for Orientation 1 (Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$).

$b_{x1}=1, b_{y1}=0$ & $b_{x2}=1, b_{y2}=0$								
	Avg SigmaXX		Avg SigmaYY		Avg SigmaZZ		Hydrostatic Stress	
	Real	Imag	Real	Imag	Real	Imag	Real	Imag
X=0	8.91E+07	3.31E-09	1.48E+07	3.10E-10	3.53E+07	1.23E-09	4.64E+07	1.62E-09
X=0.1	9.03E+07	2.82E-09	1.49E+07	2.59E-10	3.58E+07	1.05E-09	4.70E+07	1.38E-09
X=0.2	9.14E+07	3.45E-09	1.51E+07	2.91E-10	3.62E+07	1.27E-09	4.76E+07	1.67E-09
X=0.3	9.25E+07	3.25E-09	1.52E+07	2.52E-10	3.66E+07	1.19E-09	4.81E+07	1.56E-09
X=0.4	9.36E+07	3.46E-09	1.53E+07	3.47E-10	3.70E+07	1.29E-09	4.87E+07	1.70E-09
X=0.5	9.47E+07	3.29E-09	1.54E+07	2.06E-10	3.74E+07	1.19E-09	4.92E+07	1.56E-09
X=0.6	9.57E+07	3.52E-09	1.56E+07	3.30E-10	3.78E+07	1.31E-09	4.97E+07	1.72E-09
X=0.7	9.68E+07	3.51E-09	1.57E+07	3.25E-10	3.82E+07	1.30E-09	5.02E+07	1.71E-09
X=0.8	9.78E+07	3.20E-09	1.58E+07	2.16E-10	3.86E+07	1.16E-09	5.07E+07	1.52E-09
X=0.9	9.88E+07	3.51E-09	1.59E+07	3.03E-10	3.90E+07	1.30E-09	5.12E+07	1.70E-09
X=1	9.98E+07	3.64E-09	1.60E+07	3.34E-10	3.94E+07	1.35E-09	5.17E+07	1.77E-09
							4.91E+07	1.63E-09

Table A. 2: Average value of Different Stresses around dislocations with varying amount of Phase Transformation for Orientation 2 (Dislocation 1 with Burgers Vectors $b_x=1$, $b_y=0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$).

$b_{x1}=1$, $b_{y1}=0.6$ & $b_{x2}=1$ $b_{y2}=0$								
	Avg SigmaXX		Avg SigmaYY		Avg SigmaZZ		Hydrostatic Stress	
	Real	Imag	Real	Imag	Real	Imag	Real	Imag
X=0	1.18E+08	4.00E-09	6.63E+07	2.06E-09	6.26E+07	2.06E-09	8.23E+07	2.71E-09
X=0.1	1.19E+08	3.51E-09	6.69E+07	1.94E-09	6.34E+07	1.86E-09	8.33E+07	2.44E-09
X=0.2	1.21E+08	4.15E-09	6.75E+07	2.00E-09	6.41E+07	2.09E-09	8.42E+07	2.75E-09
X=0.3	1.23E+08	3.96E-09	6.80E+07	2.02E-09	6.48E+07	2.03E-09	8.51E+07	2.67E-09
X=0.4	1.24E+08	4.16E-09	6.85E+07	2.04E-09	6.55E+07	2.11E-09	8.61E+07	2.77E-09
X=0.5	1.26E+08	4.03E-09	6.91E+07	2.02E-09	6.62E+07	2.06E-09	8.69E+07	2.70E-09
X=0.6	1.27E+08	4.24E-09	6.96E+07	2.08E-09	6.69E+07	2.15E-09	8.78E+07	2.83E-09
X=0.7	1.28E+08	4.25E-09	7.01E+07	2.12E-09	6.75E+07	2.17E-09	8.87E+07	2.85E-09
X=0.8	1.30E+08	3.94E-09	7.06E+07	2.02E-09	6.82E+07	2.03E-09	8.95E+07	2.66E-09
X=0.9	1.31E+08	4.26E-09	7.11E+07	2.03E-09	6.88E+07	2.14E-09	9.04E+07	2.81E-09
X=1	1.33E+08	4.38E-09	7.16E+07	2.13E-09	6.94E+07	2.21E-09	9.12E+07	2.91E-09
							8.69E+07	2.74E-09

Table A. 3: Average value of Different Stresses around dislocations with varying amount of Phase Transformation for Orientation 3 (Dislocation 1 with Burgers Vectors $b_x=0$, $b_y=-0.6$ and Dislocation 2 with Burgers vector $b_x=1$, $b_y=0$).

$b_{x1}=0$, $b_{y1}=-0.6$ & $b_{x2}=1$, $b_{y2}=0$								
	Avg SigmaXX		Avg SigmaYY		Avg SigmaZZ		Hydrostatic Stress	
	Real	Imag	Real	Imag	Real	Imag	Real	Imag
X=0	1.76E+08	7.96E-09	-5.85E+06	7.67E-10	5.78E+07	2.45E-09	7.60E+07	3.73E-09
X=0.1	1.78E+08	7.31E-09	-5.83E+06	6.56E-10	5.86E+07	2.26E-09	7.69E+07	3.41E-09
X=0.2	1.80E+08	8.43E-09	-5.81E+06	5.17E-10	5.93E+07	2.69E-09	7.79E+07	3.88E-09
X=0.3	1.82E+08	8.12E-09	-5.79E+06	6.98E-10	6.00E+07	2.52E-09	7.88E+07	3.78E-09
X=0.4	1.84E+08	8.20E-09	-5.77E+06	4.60E-10	6.07E+07	2.63E-09	7.97E+07	3.76E-09
X=0.5	1.86E+08	8.08E-09	-5.75E+06	8.06E-10	6.14E+07	2.47E-09	8.06E+07	3.78E-09
X=0.6	1.88E+08	8.80E-09	-5.73E+06	4.86E-10	6.21E+07	2.83E-09	8.15E+07	4.04E-09
X=0.7	1.90E+08	8.32E-09	-5.71E+06	7.42E-10	6.27E+07	2.58E-09	8.24E+07	3.88E-09
X=0.8	1.92E+08	7.67E-09	-5.69E+06	8.69E-10	6.34E+07	2.31E-09	8.33E+07	3.62E-09
X=0.9	1.94E+08	8.06E-09	-5.67E+06	6.63E-10	6.40E+07	2.51E-09	8.41E+07	3.75E-09
X=1	1.96E+08	8.78E-09	-5.64E+06	6.06E-10	6.47E+07	2.78E-09	8.50E+07	4.05E-09
							8.06E+07	3.79E-09

Appendix B: MATLAB Code for Simulating Cyclic Voltammogram

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%Cyclic Voltammetry Simulation%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Based on Bard and Faulkner, Appendix B%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Orientation  b1=1,by=0,bx2=1,by2=0%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

clc;

clear all;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% CV without Stress%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%% INDEPENDENT VARIABLES %%

C    = 1.0;  % [=] mol/cm^3, initial concentration of O

D    = 1E-5; % [=] cm^2/s, O & R diffusion coefficient

Init_OP= +0.3; % [=] V, initial overpotential (relative to redox potential)

Fin_OP = -0.3; % [=] V, final overpotential (relative to redox potential)

v     = 1E-3; % [=] V/s, sweep rate

n     = 1.0;  % [=] no: of electrons transfered

alpha = 0.5;  % [=] dimensionless charge-transfer coefficient

k0    = 1E-2; % [=] cm/s, electrochemical rate constant

kc    = 1E-3; % [=] 1/s, chemical rate constant

T     = 298.15; % [=] K, temperature in Kelvin

```


%% PHYSICAL CONSTANTS %%

$F = 96485$; % [=] C/mol, Faraday's constant

$R = 8.3145$; % [=] J/mol-K, ideal gas constant

$f = F/(R*T)$; % [=] 1/V, normalized Faraday's constant at room temperature

%% SIMULATION VARIABLES %%

$L = 500$; % [=] number of iterations per t_k

$DM = 0.45$; % [=] model diffusion coefficient

%% DERIVED CONSTANTS %%

$t_k = 2*(Init_OP - Fin_OP)/v$; % [=] s, characteristic exp. time

$Dt = t_k/L$; % [=] s, delta time

$Dx = \sqrt{D*Dt/DM}$; % [=] cm, delta x

$j = \text{ceil}(4.2*L^{0.5})+5$; % number of boxes

%% REVERSIBILITY PARAMETERS %%

$ktk = kc*t_k$ % dimensionless kinetic parameter

$km = ktk/L$ % normalized dimensionless kinetic parameter

$\Lambda = k_0/(D*f*v)^{0.5}$ % dimensionless reversibility parameter

%% PRE-INITIALIZATION %%

$k = 0:L$; % time index vector

```

t = Dt * k;          % time vector

eta1 = Init_OP - v*t; % overpotential vector, negative scan

eta2 = Fin_OP + v*t;  % overpotential vector, positive scan

eta = [eta1(eta1>Fin_OP) eta2(eta2<=Init_OP)]'; % overpotential scan, both directions

Enorm = eta*f;        % normalized overpotential

kf = k0.*exp( -alpha *n*Enorm); % [=] cm/s, fwd rate constant

kb = k0.*exp((1-alpha)*n*Enorm) ;% [=] cm/s, rev rate constant

O = C*ones(L+1,j); % [=] mol/cm^3, concentration of O

R = zeros(L+1,j); % [=] mol/cm^3, concentration of R

JO = zeros(1,L+1); % [=] mol/cm^2-s, flux of O at the surface

%% START SIMULATION %%

% i1 = time index. i2 = distance index

for i1 = 1:L

% Update bulk concentrations of O and R

    for i2 = 2:j-1

        O(i1+1,i2) = O(i1,i2) + DM*(O(i1,i2+1)+O(i1,i2-1)-2*O(i1,i2));

        R(i1+1,i2) = R(i1,i2) + DM*(R(i1,i2+1)+R(i1,i2-1)-2*R(i1,i2)) ...

            - km * R(i1,i2);

```

```

end

% Update flux

JO(i1+1) = ( kf(i1+1).*O(i1+1,2) - kb(i1+1).*R(i1+1,2) ) ./ (1 + Dx/D*(kf(i1+1) + kb(i1+1)))
);

% Update surface concentrations

O(i1+1,1) = O(i1+1,2) - JO(i1+1)*(Dx/D);

R(i1+1,1) = R(i1+1,2) + JO(i1+1)*(Dx/D) - km*R(i1+1,1);

end

% Calculate current density, Z, from flux of O

Z = -n.*F.*JO/10; % [=] A/m^2 -> mA/cm^2, current density

%% PLOT RESULTS %%

% Sometimes length(eta) = length(Z) + 1. If this is the case, truncate last value

if length(eta) > length(Z)

    eta = eta(1:end-1);

end

plot(eta,Z,':b','LineWidth',1.2)

xlabel('Overpotential (V)'), ylabel('Current density (mA/cm^2)')

hold on

```

%%%%%%%%Cyclic Voltammetry Simulation%%%%%%%%

%%%%%%%% Based on Bard and Faulkner, Appendix B%%%%%%%%

clc;

clear all;

%%%%%%%% CV with Phase Transformation%%%%%%%%

%% INDEPENDENT VARIABLES %%

C = 1.0; % [=] mol/cm³, initial concentration of O

D = 1E-5; % [=] cm²/s, O & R diffusion coefficient

Init_OP= +0.3; % [=] V, initial overpotential (relative to redox potential)

Fin_OP = -0.3; % [=] V, final overpotential (relative to redox potential)

v = 1E-3; % [=] V/s, sweep rate

n = 1.0; % [=] no: of electrons transfered

alpha = 0.5; % [=] dimensionless charge-transfer coefficient

k0 = 1E-2; % [=] cm/s, electrochemical rate constant

kc = 1E-3; % [=] 1/s, chemical rate constant

T = 298.15; % [=] K, temperature in Kelvin

%% PHYSICAL CONSTANTS %%

F = 96485; % [=] C/mol, Faraday's constant

```

R    = 8.3145; % [=] J/mol-K, ideal gas constant

f    = F/(R*T); % [=] 1/V, normalized Faraday's constant at room temperature

%% SIMULATION VARIABLES %%

L    = 500; % [=] number of iterations per t_k

DM    = 0.45; % [=] model diffusion coefficient

%% DERIVED CONSTANTS %%

tk    = 2*(Init_OP-Fin_OP)/v; % [=] s, characteristic exp. time

Dt    = tk/L; % [=] s, delta time

Dx    = sqrt(D*Dt/DM); % [=] cm, delta x

j    = ceil(4.2*L^0.5)+5; % number of boxes

%% REVERSIBILITY PARAMETERS %%

ktk    = kc*tk; % dimensionless kinetic parameter

km    = ktk/L; % normalized dimensionless kinetic parameter

Lambda = k0/(D*f*v)^0.5; % dimensionless reversibility parameter

%% PRE-INITIALIZATION %%

k    = 0:L; % time index vector

t    = Dt * k; % time vector

eta1 = Init_OP - v*t; % overpotential vector, negative scan

```

```

eta2 = Fin_OP + v*t; % overpotential vector, positive scan

eta = [eta1(eta1>Fin_OP) eta2(eta2<=Init_OP)]'; % overpotential scan, both directions

pt(length(eta),1)=0;

for index=1:length(eta)

    if eta(index,1) < 0

        pt(index,1)=0;

    end

    if eta(index,1) >30.283e-3

        pt(index,1)=1;

    end

    if eta(index,1)>0 & eta(index,1)<30.283e-3

        aaa=6;

        ccc=1.5;

        pt(index,1) = 1./(1+exp(-aaa.*(100.*eta(index,1)-ccc)));

    end

end

%Interpolating Stresses

gx=0:0.1:1;

```

```

gy=[4.64 4.7 4.76 4.81 4.87 4.92 4.97 5.02 5.07 5.12 5.17];

%%%%%%For b1=1,by=0.6,bx2=1,by2=0%%%%

%%gy=[8.23 8.33 8.42 8.51 8.61 8.69 8.78 8.87 8.95 9.04 9.12 ];%%

%%%%%%%% For b1=0,by=-0.6,bx2=1,by2=0%%%%

%gy=[7.59752 7.69355 7.78807 7.88114 7.97283 8.06320 8.15230 8.24019 8.32690 8.41250
8.49702];%

vq1 = interp1(gx,gy,pt);

Enorm = eta*f;      % normalized overpotential

kf = k0.*exp( -alpha *n*(Enorm-(vq1.*10^3/(R*T)))); % [=] cm/s, fwd rate constant

kb = k0.*exp((1-alpha)*n*(Enorm-(vq1.*10^3/(R*T)))); % [=] cm/s, rev rate constant

O = C*ones(L+1,j); % [=] mol/cm^3, concentration of O

R = zeros(L+1,j); % [=] mol/cm^3, concentration of R

JO = zeros(1,L+1); % [=] mol/cm^2-s, flux of O at the surface

%% START SIMULATION %%

% i1 = time index. i2 = distance index

for i1 = 1:L

    % Update bulk concentrations of O and R

    for i2 = 2:j-1

        O(i1+1,i2) = O(i1,i2) + DM*(O(i1,i2+1)+O(i1,i2-1)-2*O(i1,i2));

```

```

R(i1+1,i2) = R(i1,i2) + DM*(R(i1,i2+1)+R(i1,i2-1)-2*R(i1,i2)) ...

- km * R(i1,i2);

end

% Update flux

JO(i1+1) = ( kf(i1+1).*O(i1+1,2) - kb(i1+1).*R(i1+1,2) ) ./ (1 + Dx/D*(kf(i1+1) + kb(i1+1))

);

% Update surface concentrations

O(i1+1,1) = O(i1+1,2) - JO(i1+1)*(Dx/D);

R(i1+1,1) = R(i1+1,2) + JO(i1+1)*(Dx/D) - km*R(i1+1,1);

end

% Calculate current density, Z, from flux of O

Z = -n.*F.*JO/10; % [=] A/m^2 -> mA/cm^2, current density

%% PLOT RESULTS %%

% Sometimes length(eta) = length(Z) + 1. If this is the case, truncate last value

if length(eta) > length(Z)

    eta = eta(1:end-1);

end

hold on;

plot(eta,Z,'-k','LineWidth',1.5)

```


hold on

%%%%%%%%%%Cyclic Voltammetry Simulation%%%%%%%%%%

%%%%%%%%% Based on Bard and Faulkner, Appendix B%%%%%%%%

clc;

clear all;

%%%%%%%%%% CV without Phase Transformation%%%%%%%%%%

%% INDEPENDENT VARIABLES %%

C = 1.0; % [=] mol/cm³, initial concentration of O

D = 1E-5; % [=] cm²/s, O & R diffusion coefficient

Init_OP= +0.3; % [=] V, initial overpotential (relative to redox potential)

Fin_OP = -0.3; % [=] V, final overpotential (relative to redox potential)

v = 1E-3; % [=] V/s, sweep rate

n = 1.0; % [=] no: of electrons transfered

alpha = 0.5; % [=] dimensionless charge-transfer coefficient

k0 = 1E-2; % [=] cm/s, electrochemical rate constant

kc = 1E-3; % [=] 1/s, chemical rate constant

T = 298.15; % [=] K, temperature in Kelvin

%% PHYSICAL CONSTANTS %%

```

F    = 96485; % [=] C/mol, Faraday's constant

R    = 8.3145; % [=] J/mol-K, ideal gas constant

f    = F/(R*T); % [=] 1/V, normalized Faraday's constant at room temperature

%% SIMULATION VARIABLES %%

L    = 500; % [=] number of iterations per t_k

DM    = 0.45; % [=] model diffusion coefficient

%% DERIVED CONSTANTS %%

tk    = 2*(Init_OP-Fin_OP)/v; % [=] s, characteristic exp. time

Dt    = tk/L; % [=] s, delta time

Dx    = sqrt(D*Dt/DM); % [=] cm, delta x

j    = ceil(4.2*L^0.5)+5; % number of boxes

%% REVERSIBILITY PARAMETERS %%

ktk    = kc*tk; % dimensionless kinetic parameter

km    = ktk/L; % normalized dimensionless kinetic parameter

Lambda = k0/(D*f*v)^0.5; % dimensionless reversibility parameter

%% PRE-INITIALIZATION %%

k = 0:L; % time index vector

t = Dt * k; % time vector

```

```

eta1 = Init_OP - v*t; % overpotential vector, negative scan

eta2 = Fin_OP + v*t; % overpotential vector, positive scan

eta = [eta1(eta1>Fin_OP) eta2(eta2<=Init_OP)]'; % overpotential scan, both directions

Enorm = eta*f; % normalized overpotential

kf = k0.*exp( -alpha *n*(Enorm-(4.64*10^3/(R*T)))); % [=] cm/s, fwd rate constant

kb = k0.*exp((1-alpha)*n*(Enorm-(4.64*10^3/(R*T)))); % [=] cm/s, rev rate constant

%% Code Lines For other Orientations%%

%% For b1=0,by=0.6,bx2=1,by2=0%%

%kf = k0.*exp( -alpha *n*(Enorm-(8.23*10^3/(R*T)))); % [=] cm/s, fwd rate constant

%kb = k0.*exp((1-alpha)*n*(Enorm-(8.23*10^3/(R*T)))); % [=] cm/s, rev rate constant

%% For b1=0,by=-0.6,bx2=1,by2=0%%

%kf = k0.*exp( -alpha *n*(Enorm-(7.59752*10^3/(R*T)))); % [=] cm/s, fwd rate constant

%kb = k0.*exp((1-alpha)*n*(Enorm-(7.59752*10^3/(R*T)))); % [=] cm/s, rev rate constant

O = C*ones(L+1,j); % [=] mol/cm^3, concentration of O

R = zeros(L+1,j); % [=] mol/cm^3, concentration of R

JO = zeros(1,L+1); % [=] mol/cm^2-s, flux of O at the surface

%% START SIMULATION %%

% i1 = time index. i2 = distance index

```

```
for i1 = 1:L
```

```
    % Update bulk concentrations of O and R
```

```
    for i2 = 2:j-1
```

```
        O(i1+1,i2) = O(i1,i2) + DM*(O(i1,i2+1)+O(i1,i2-1)-2*O(i1,i2));
```

```
        R(i1+1,i2) = R(i1,i2) + DM*(R(i1,i2+1)+R(i1,i2-1)-2*R(i1,i2)) ...
```

```
        - km * R(i1,i2);
```

```
    end
```

```
    % Update flux
```

```
    JO(i1+1) = ( kf(i1+1).*O(i1+1,2) - kb(i1+1).*R(i1+1,2) ) ./ (1 + Dx/D*(kf(i1+1) + kb(i1+1)))
);
```

```
    % Update surface concentrations
```

```
    O(i1+1,1) = O(i1+1,2) - JO(i1+1)*(Dx/D);
```

```
    R(i1+1,1) = R(i1+1,2) + JO(i1+1)*(Dx/D) - km*R(i1+1,1);
```

```
end
```

```
% Calculate current density, Z, from flux of O
```

```
Z = -n.*F.*JO/10; % [=] A/m^2 -> mA/cm^2, current density
```

```
%% PLOT RESULTS %%
```

```
% Sometimes length(eta) = length(Z) + 1. If this is the case, truncate last value
```

```
if length(eta) > length(Z)
```

```

    eta = eta(1:end-1);

end

plot(eta,Z,'-r','LineWidth',1.5)

hold on

legend('w/o stress','phase transformation','no phase trasnformation')

title('Molar Volume= 1e-4')

%%%Displaying Grey Box%%%%%%%%%%

gray = [0.9 0.9 0.9];

patch([0 30.283e-3 30.283e-3 0],[-2.5 -2.5 1.5 1.5],gray,'EdgeColor','none')

set(gca,'children',flipud(get(gca,'children')))

%%%%%%%%%%

```