

$\text{Li}_2\text{CoSiO}_4$ as an Advanced Cathode Material for Next Generation Lithium-Ion Batteries

**A Project Report Submitted
As part of the requirements for the degree of**

MASTER OF SCIENCE

By

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To the
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INDIAN INSTITUTE OF TECHNOLOGY HYDERABAD

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of Dr. Surendra K. Martha.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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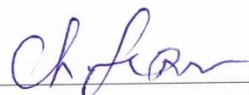
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Approval Sheet

This thesis entitled "**Li₂CoSiO₄ as an Advanced Cathode Material for Next Generation Lithium-Ion Batteries**" by **Mr. Sourav Ghosh** is approved for the degree of Master of Science from IIT Hyderabad.



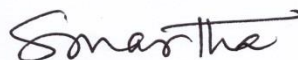
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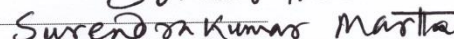
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Abstract

Now a day, one of the biggest challenges for the mankind is to harvest energy from the renewable energy sources like solar, wind and store it for different applications. Battery is one of the successful energy devices which can store energy. Lithium ion battery which has largest energy density of 120- 200 Wh/Kg is the most promising secondary battery in the market today. Current, research efforts in electrochemical energy storage is directed towards achieving higher energy density with reduced cost and improved thermal safety. State-of-the-art lithium-ion cells use layered transition metal (TM) oxides (LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$ etc.), or Phosphates (LiFePO_4) Mn based spinels as cathodes (LiMn_2O_4) and graphitic carbon as anode. The nominal capacities of most of these cathodes are range between 140-180 mAhg^{-1} when cycled up to 4.2 V. This is only half the specific capacity of graphite anode (372mAhg^{-1}). Besides only $\frac{1}{2}$ Lithium from TM oxides or 1 Li from phosphates could be intercalated or deintercalated from the material. Thus, there has been an intense research activity in the last decade to develop high capacity (multi electron capacity), high energy cathode materials for lithium-ion batteries.

Recently, polyanionic type lithium metal silicate cathode materials has received much importance because of their high capacity and stability over the other cathode materials in lithium ion battery. Phosphates and silicates are the most stable materials for Li-ion battery. But only $1 e^-$ can be removed from the system which can lead to the capacity of 160 mAh/g for phosphate systems. Silicates are advantageous over phosphate due to high capacity of $\sim 330 \text{mAh/g}$ (2 electron capacity) and high operating voltage $> 4.3 \text{ V}$, so that high energy density (1400Wh/Kg) could be achieved for the silicates. Among the silicates, $\text{Li}_2\text{CoSiO}_4$ is advantageous over its Fe and Mn counterparts because of high operating voltage. But practically less capacity and cycle life is achieved because of poor conductivity and structural instability during charge-discharge of silicates. These factors are also leading to poor C rate performance and high irreversible capacity. Because of which silicates are not able make use of practical lithium-ion batteries. So our goal is to improve the electrochemical performance of the material by synthesising $\text{Li}_2\text{CoSiO}_4$ in nanoscale, eliminating electrochemically inert additive through electrode architectures.

The use of nanoparticles will enable us high C rate performance whereas electrode architecture will improve the electronic conductivity of the material. The $\text{Li}_2\text{CoSiO}_4$ materials have been synthesized by various synthetic routes such as Solid State, Polyol and Solvothermal syntheses. Further, optimize synthetic conditions for best electrochemical performance and better stability. XRD, SEM, BET, TGA were used for structural and physical characterization of the samples. Electrochemical performances were characterized by galvanostatic charge-discharge, CV, EIS studies.

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1. Motivation

Over the last decades energy has become the central focus of the modern economy. The access to energy is very critical to the wealth, life style and image of every country. The effect of globalization, population increase and rising consumer demands across developed and developing countries have resulted in an exponential increase in energy consumption. The biggest challenges for the mankind are to harvest energy from the renewable energy sources and store it for different applications because of depletion of non-renewable energy sources day by day. Renewable energy sources like solar and wind provides time-varying, somewhat unpredictable energy supply, which must be captured and stored until demanded. Battery is one of the energy devices which can store these energies and do the job successfully when needed. Battery is one of the successful energy devices which can store energy. Lithium ion battery which has largest energy density of 120- 200 Wh/Kg is the most promising secondary battery in the market today. Current, research efforts in electrochemical energy storage is directed towards achieving higher energy density with reduced cost and improved thermal safety. State-of-the-art lithium-ion cells use layered transition metal (TM) oxides (LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$ etc.), or Phosphates (LiFePO_4) Mn based spinels as cathodes (LiMn_2O_4) and graphitic carbon as anode. The nominal capacities of most of these cathodes are range between 140-180 mAhg^{-1} when cycled up to 4.2 V. This is only half the specific capacity of graphite anode (372mAhg^{-1}). Besides only $\frac{1}{2}$ Lithium from TM oxides or 1 Li from phosphates could be intercalated or deintercalated from the material. Thus, there has been an intense research activity in the last decade to develop high capacity (multi electron capacity), high energy cathode materials for lithium-ion batteries.

2. Thermodynamics of Li-ion battery³⁴

Batteries are electrochemical devices which stores energy for future use. A battery is composed of a positive and negative electrode. The positive and negative electrodes are separated by separator with an electrolyte which conducts ions from positive electrode to negative and vice-versa. The potential difference between the two electrodes drives the ions from one electrode to the other. The current collectors transfer the electron from negative electrode to positive electrode through an external circuit. It is the redox reaction taking place between cathode and anode material producing the electrical energy. The driving force for any reaction to occur is in expense of Gibb's free energy.

The basic thermodynamic equation for a reversible electrochemical reaction is given as followed:

$$\Delta G = \Delta H - T\Delta S$$

Where, ΔG is the Gibbs free energy or the energy that can be provided for useful work. ΔH is the enthalpy, which is the entire energy released by the reactions. ΔS are the entropy, and T is the absolute temperature, while $T\Delta S$ represents the heat dissipation with random movement of materials.

Since ΔG represents the net useful work energy available from the reactions, the net available electrical energy from the reactions can be given by the following formula:

$$E = -\frac{\Delta G}{nF}$$

Where, E is the e.m.f. of cell, ΔG is the Gibbs free energy, n is number of electron transfer taking place during redox reaction and F is faraday constant (96487 C/mol).

3. Why lithium ion battery?

In recent times, many rechargeable batteries like lead-acid battery, nickel-cadmium battery, metal hydride battery and lithium ion battery etc. are available in the market. Among all these, lithium ion battery is one of the best choices of the people because:

- i) Lightest metal: Li is the lightest metal in the periodic table. Atomic mass of Li is 6.941 gm/mole.
- ii) Electrochemical potential: It has highest electrochemical potential i.e. reduction potential, $\text{Li}^+ + e \rightarrow \text{Li}$ (-3.06 V). This leads to high open-circuit-voltage (OCV) compare to other secondary batteries.
- iii) High Energy Density: The above two points leads to high energy density of Li-ion battery. Energy density is the energy storage per unit weight or per unit volume in the battery.

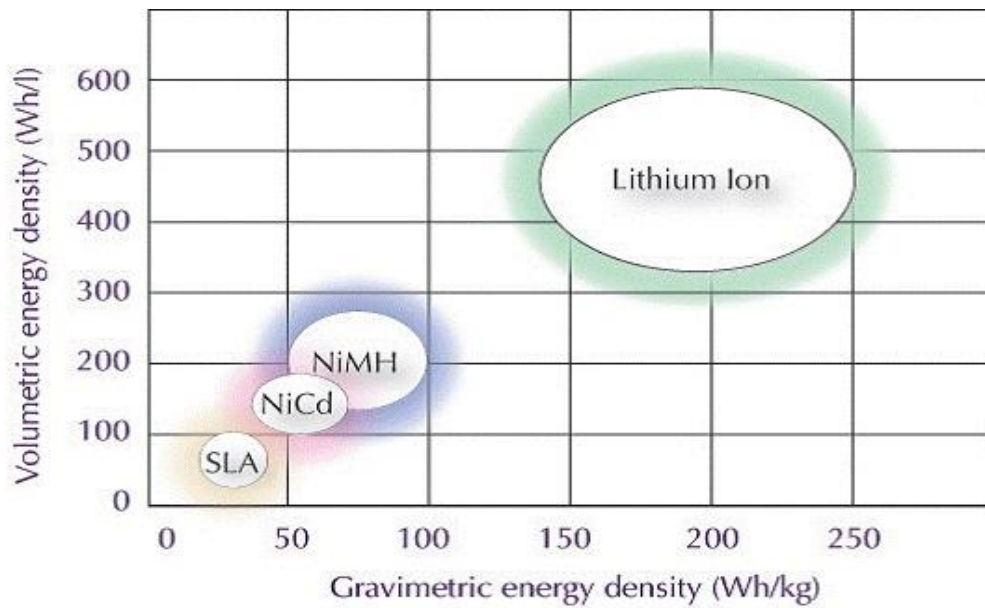


Figure 1: Comparison of energy density for different types of batteries [Adapted from J.M. Tarascon, M. Armand, Nature, 414(2011) 359-367]

- iv) No memory effect: Memory effect is an effect observed in rechargeable batteries that causes them to hold less charge. Memory effect describes the situation in which the batteries gradually lose their capacity after repeated recharge after being partially discharged. The batteries appear to remember the smaller capacity. No memory effect is observed for lithium-ion battery.
- v) Relatively low self-discharge: Lithium-ion battery has up to 10 % self-discharge per month.

4. What is lithium ion battery?

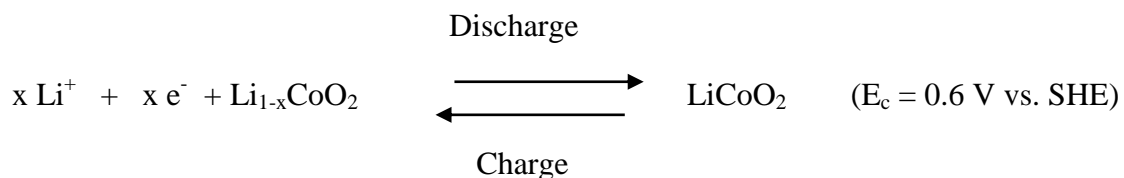
The term “lithium-ion battery” refers to a diverse family of battery chemistries. All Li-ion batteries use a process known as intercalation, in which lithium ions are incorporated into the structure of the electrode material. Lithium ions move from the positive to the negative electrode during charging and from the negative to the positive electrode as the battery is discharged. The cathode, the anode and the electrolyte are the main components of lithium ion battery.

4.1 Operating principle

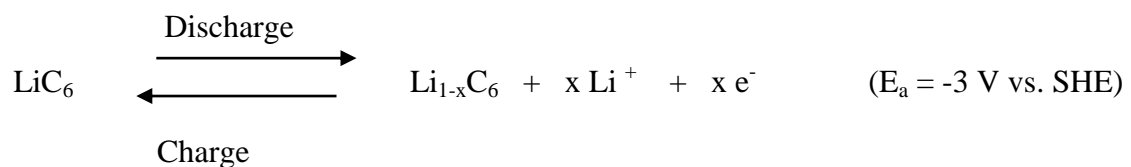
In general, a lithium ion battery is composed of a cathode, an anode and a separator soaked in an electrolyte. During charging and discharging, reversible exchange of Li-ion takes place between cathode and anode. The electrolyte used is an organic electrolyte containing any Li-ion salt like LiPF_6 , LiAsF_6 dissolved in organic solvents like ethylene carbonate (EC) and dimethyl carbonate (DMC). So, reversible exchange of Li-ion becomes more feasible and other Li^+ ion is not there to interact with either cathode or anode material. The ionic conductivity of these mixtures is about two orders of magnitude lower than that of aqueous alkaline electrolytes but is high enough to make practical batteries for use at or above room temperature. Actually, even at 0°C the ionic conductivity of $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ for these electrolytes suffices for practical batteries. The conductivity however varies a bit with temperature and ranges from $0.23 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at -40°C to $1.46 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 40°C for LiPF_6 dissolved in 1:1 volume mixture of EC: DMC. The material which used as a cathode material should contain Li-ion because during charging Li ion deintercalate from cathode to anode material. And reverse reaction takes place during discharging. Some of the established cathode materials are LiMO_2 , (M stands for transition metals such as Fe, Mn, Co, Ni etc.), LiMn_2O_4 , LiMPO_4 , and Lithiated graphite is used as anode.

The electrochemical reaction that is taking place during charging and discharging are shown below:

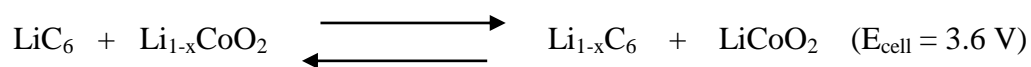
At the positive electrode (at cathode):



At the negative electrode (at anode):



Accordingly, the net cell reactions during its charge-discharge process are:



Schematically, the lithium ion battery can be represented as:

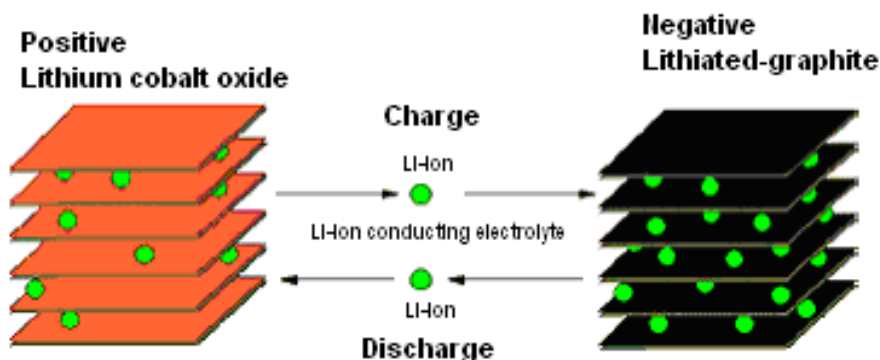


Figure 2: Schematic representation of lithium ion battery

4.2 Cathodes material³³

The cathode is the source of the lithium ion. The key requirements for a material to be successfully used as a cathode in a rechargeable lithium battery are as follows.

- i) The material contains a readily redox ion, for example a transition metals.
- ii) The materials react with lithium in reversible manner.
 - a) This dictates an intercalation-type reaction in which the host structure essentially does not change as lithium is added.
- iii) The material reacts with lithium with a high free energy of reaction.
 - a) High capacity, preferably at least one lithium per transition metal.
 - b) High voltage may be around 4 V.
 - c) This leads to high energy density.
- iv) The material reacts with lithium very rapidly both on insertion and removal. This leads to high power density, which is needed to replace Ni/Cd battery or for batteries that can be recharged using HEV regenerative braking (High C rate application).
- v) The material should be a good electronic conductor.
 - a) This allows for the easy addition or removal of electrons during the electrochemical reaction.
 - b) This minimizes the need for inactive conductive diluents, which take away from the overall energy density.

- c) This allows for reaction at all contact points between the cathode active material and the electrolyte rather than at ternary contact points between the cathode active material, the electrolyte, and the electronic conductor (such as carbon black).
- vi) The material is stable, i.e., not change structure or otherwise degrade, to over discharge and overcharge.
- vii) The material is low cost.
- viii) The material should be eco- friendly.

In the light of the above mentioned points, several materials have been studied as cathode material like layered oxide, spinel, olivine, and discussed briefly below.

Layered oxide (LiMO₂, and its derivatives):

The report of layered LiCoO₂ by Goodenough et al¹, cyclable up to 4 V, used in many commercially available Li-ion batteries. LiCoO₂ is easily synthesized by solid-state reaction in the temperature range between 850°C and 1000°C over several hours. LiCoO₂ is isostructural to α-NaFeO₂². It has a rhombohedral structure where Li and Co fill alternative layers of edge-sharing octahedral sites in a close-packed oxygen array (Li in 3b, Co in 3a and O in 6a sites) with R3m space-group¹. Such a structure provides a two-dimensional diffusion path for Li⁺-ions in the LiCoO₂ framework as shown in Figure 3

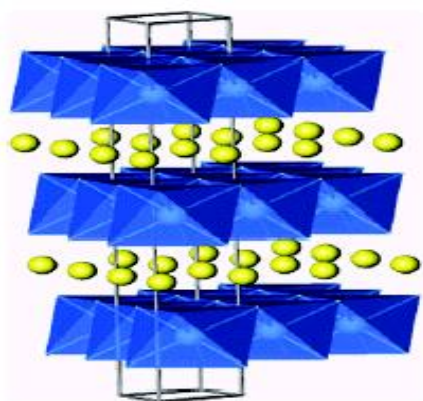


Figure 3: Structure of layered LiMO₂ (M = Co, Ti, Ni)

Removal of Li in Li_xCoO_2 from $x = 1$ to $x = 0.1$ yields a capacity value of 274 mAh g^{-1} . But, in practice, delithiation in LiCoO_2 is restricted to $x = 0.5$, that corresponds to 4.2 V vs. Li/Li^+ . These authors report, that Li removal up to $x = 0.5$ results in an increase in interlayer distance and a decrease thereafter. Complete delithiation in LiCoO_2 brings about 6-8 % reduction in unit cell volume, which is detrimental to electrode reversibility. It is however, reported that CoO_2 structure can accommodate lithium up to 90-95 % by electrochemical reduction at a low rate³, suggesting both the phase and volume changes to be reversible. Hence, dissolution of cobalt at high potentials in the electrolyte and the resulting structural changes cause capacity fade upon cycling above 4.2 V . Therefore, cycling of LiCoO_2 cathode is generally restricted to only up to 4.2 V . However, several efforts to cycle LiCoO_2 cathode beyond 4.2 V are being expended to extract extra capacity from LiCoO_2 so as to increase the energy density of the Li-ion cells.

Several efforts have been put to synthesise substituted LiCoO_2 i.e. $\text{LiM}_x\text{Co}_{1-x}\text{O}_2$ which are isostructural with LiCoO_2 to develop more promising cathode material in terms of energy density, cost, safety etc. Some of the reported literatures are Ni^4 , Al^5 , Mg^6 , Fe^7 , Mn^8 , Ti^9 , Zn^{10} , Cr^{11} , B^{12} and Rh^{13} .

Substituting Ni in LiCoO_2 is studied by several authors using different methods due to its significance in increasing the capacity. Substituting Ni metal in LiCoO_2 is found to favour its electrochemical performance up to $y = 0.2$. But, a high level of substitution is found to degrade its electrochemical performance due to cation mixing, i.e. Ni occupying some of the Li sites in the Li layer.

Whenever Al substitution comes into picture, mainly two effects are being observed, first thing is increase in voltage by 0.15V - 0.20V when LiCoO_2 is substituted by $\text{LiAl}_{0.25}\text{Co}_{0.75}\text{O}_2$, the other one is capacity fading in the Al substituted LiCoO_2 . So the former one is advantage and the latter one is the disadvantage. It is suggested that a higher capacity fade in Al-substituted samples in relation to LiCoO_2 is due to a larger local structural-distortion during Li deintercalation. Hence, Al-substitution into LiCoO_2 is interesting because of its higher potential even if capacity fade is lower in LiCoO_2 .

Tukamoto et al studied Mg substituted LiCoO₂. It has been found that when low concentration of Mg is used i.e. when Li sites are occupied by Mg²⁺, then the conductivity of the material is decreased. But at higher concentration when the Mg²⁺ would occupy the Co³⁺ site then conductivity increases substantially. Mg-substituted compounds exhibit electrochemical properties similar to unsubstituted compound in terms of reversibility, but their capacity values are lower due to the lower Co³⁺-concentration. Also, Mg-substituted compounds exhibit single phase during the charge-discharge cycles, which is seminal to long-term performance.

Fe-substitution in LiCoO₂ is reported by Kobayashi et al. It is interesting to substitute Fe for Co because Fe is cheaper and environmentally friendly while Co is both toxic and costly. But, Fe-substitution degrades the electrochemical activity of LiCoO₂ due to its tendency to occupy Li-sites in the Li-layer.

LiNiO₂ is cheaper and less toxic than LiCoO₂. The specific capacity obtained for LiNiO₂ is also higher than LiCoO₂. However, LiNiO₂ needs to be synthesized carefully owing to the difficulties involved in oxidation of Ni²⁺ to Ni³⁺. The structural aspects and the electrochemical behavior of LiNiO₂ are reviewed in the literature¹⁴. Both LiCoO₂ and LiNiO₂ exhibit high voltages and facilitate Li-diffusion kinetics. LiNiO₂ is attractive because of cheaper Ni but the safety due to thermal instability of fully-charged LiNiO₂ is a concern. In order to overcome this problem, substitution of Ni by other ions, such as Al¹⁵, Cr¹⁶, Mg¹⁷, Ca¹⁸ is reported.

Mg-substitution in LiNiO₂ increases its conductivity by about two orders due to hole formation. Single-phase deintercalation is reported to favor high-rate capability and good cyclability with a specific capacity value of 152 mAh g⁻¹.

The substitution of Ni site with Co has been studied extensively because this material will have the combined property of both LiCoO₂ and LiNiO₂, namely, high structural stability of LiCoO₂ and high capacity of LiNiO₂. The presence of 30 % Co is mandatory to stabilize the layered structure with no Ni²⁺ in the Li-layers, in order to facilitate good electrochemical behavior with first discharge capacity nearly equal to LiNiO₂ and the cyclability comparable to LiCoO₂.

Some of the other lithium metal oxides which have been studied are LiMnO_2 ¹⁹ and its derivatives²⁰, LiFeO_2 ²¹, LiVO_2 etc. LiMnO_2 is a material of interest for Li-ion cells because Mn is both cheaper and safer in relation to Co in LiCoO_2 . The theoretical capacity expected for this layered LiMnO_2 is 280 mAh/g. bimetallic substitution into LiMnO_2 is also reported by Ohzuku et al.^{20c}. These authors used Ni- and Co-substituents resulting in $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ compound, which is also studied by several groups²⁰. This material shows a zero volume change up to a deintercalation of $0.67 \text{ Li}^+ \text{ mol}^{-1}$. Hence, this material is promising for advanced Li-ion cells. Sun et al.^{20f} reported $\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.3}\text{Mn}_{0.57}]\text{O}_2$, which gives a stable capacity of 190 mAh g^{-1} when cycled between 2 V and 4.6 V. Recently, $\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$ (LMR-NMC)³⁵ exhibited capacities close to the 280 mAhg^{-1} at a cut off potential of 4.9 V can be achieved for the electrodes. Further, CNF additive electrodes to LMR-NMC electrode behave reversibly for hundreds of cycles with only minor loss in capacity.

LiMn_2O_4 and its derivatives:

LiMn_2O_4 was first introduced into the commercial cells as early as in 1996²². But the poor performance of LiMn_2O_4 directed research and development efforts in improving its characteristics. LiMn_2O_4 crystallizes in space-group $\text{Fd}3\text{m}$ with Li and Mn, respectively, occupying 8a tetrahedral sites and 16d octahedral sites of the cubic-close-packed oxygen array²³. In the framework, MO_6 octahedral share edges to build a rigid 3-dimensional network with open interconnected channels in the $\langle 110 \rangle$ directions where Li^+ -ions are present (Fig. 04). Li^+ -ions are mobile within these channels along the 8a-16c-8a path.

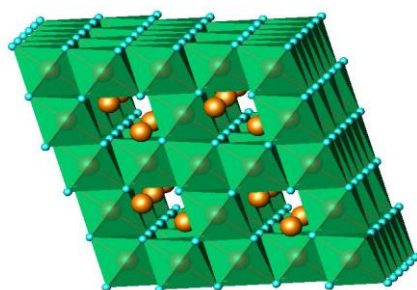


Figure 4: Schematic representation of cubic LiMn_2O_4

Among many cathode candidates, LiMn_2O_4 has been considered as one of potential candidates for used as a cathode material in lithium ion battery due to its advantages like low cost, abundance, safety etc. Capacity fade in LiMn_2O_4 is proposed to be due to the Mn dissolution into the electrolyte, essentially in the case of fluorinated salts, which generate HF^{24} . Mn dissolution is proposed to originate from the dis-proportionating of $^{25}\text{Mn}^{3+}$ as follows.



Many authors have addressed this capacity fade and have attempted to mitigate Mn-dissolution by surface coating of LiMn_2O_4 particles with different oxides²⁶.

Substitution with cations of oxidation states ≤ 3 results in a decreased 4 V-capacity window due to decrease in the Mn^{3+} -content but improves the cyclability. Hence, an optimum amount of substitution is desired to provide high capacity with good cyclability. Heavily-substituted Mn-spinels, namely $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ($\text{M} = \text{Fe}, \text{Cr}, \text{Ni}, \text{Co}, \text{Cu}$ and their mixtures), may offer high out-put voltages by taking advantage of the redox couple of the substituted cation. West et al.²⁷ examined substituted spinels and found some of the Co-substituted spinels, namely $\text{Li}_2\text{Co}_{0.8}\text{Mn}_{3.2}\text{O}_8$ and LiCoMnO_4 , to be attractive. In these compounds, $\text{Co}^{3+}/\text{Co}^{4+}$ couple creates a discharge plateau at about 5 V along with the 4 V plateau for the $\text{Mn}^{3+}/\text{Mn}^{4+}$. The capacities obtained for these materials are 135 and 105 mAh g^{-1} , respectively.

Lithium iron phosphate (LiFePO_4) i.e. olivine cathode material²⁸:

In recent years, LiFePO_4 (lithium iron phosphate) with a phospho-olivine structure has emerged as a promising cathode material for lithium-ion batteries. Its high theoretical specific capacity (280 mAh g^{-1}), flat voltage at 3.4 V, low-cost and safety make it a promising material for lithium-ion cells. Structure of LiFePO_4 is shown in Figure 5

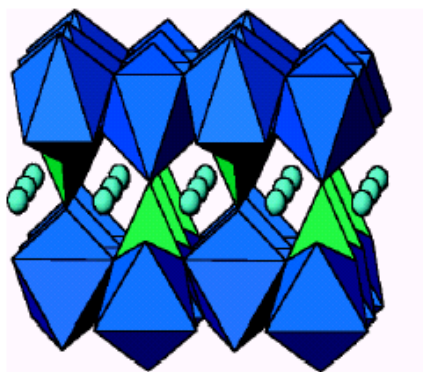


Figure 5: Structure of LiFePO₄

This is the first cathode material with potentially low cost and plentiful elements and also environmentally benign that could have a major impact in electrochemical energy storage. For LiFePO₄, the discharge potential is about 3.4 V vs lithium and no obvious capacity fading was observed even after several hundred cycles. LiFePO₄ can be synthesised by several methods like high temperature hydrothermal reaction, sol-gel technique etc. These olivine type polyanionic type cathode materials are very poorly conductive, so on carbon coating it has been observed that the conductivity has increased significantly and thus electrochemical performance has increased. In the recent times LiMnPO₄³⁶ and LiMn_{0.8}Fe_{0.2}PO₄³⁷ have shown to potential candidates for high energy cathode materials.

Table: Some of the important cathode materials and their performance characteristics.

Compound	Average Potential (V)	Specific capacity (mAh g ⁻¹)	Cost of the Metal present (\$ kg ⁻¹)	Structural stability	Cycle life	Rate capability	Nature of the discharge curve	Toxicity
LiCoO ₂	3.9	160	90	Fair	Good	Good	Flat	High
LiAl _{0.25} Co _{0.75} O ₂	3.95	127	--	Poor	Poor	Poor	Flat	High
LiMg _{0.05} Co _{0.95} O ₂	3.9	143	--	Fair	Fair	Good	Flat	High
LiNiO ₂	3.85	200	50	Poor	Fair	Good	Sloping	Fair
LiNi _{0.8} Co _{0.2} O ₂	3.7	175	--	Fair	Good	Good	Sloping	Fair
LiAl _{1/4} Ni _{3/4} O ₂	3.7	170	--	Fair	Good	Fair	Flat	Fair
LiNi _{0.5} Mn _{0.5} O ₂	3.7	160	--	Fair	Good	Fair	Sloping	Fair
LiFePO ₄	3.2	160	100	Good	Good	Poor	Flat	Low
LiMn ₂ O ₄	4.0	110	75	Poor	Fair	Good	Flat	Low
LiNi _{0.5} Mn _{1.5} O ₄	4.6	135	100	Fair	Good	Good	Flat	Fair
LiMn _{1/3} Co _{1/3} Ni _{1/3} O ₂	4.0	200	90	Fair	Fair	Good	Flat	Fair
LiMn _{0.53} Ni _{0.17} Co _{0.1} O ₂	3.7	>250	>250	Fair	Fair	Fair	Sloping	Low

4.3 Anode materials³¹

Initially Li metal was used as an anode in LIB. Later Sony Company of Japan introduced graphite as anode. Pure Li metal, due to a very high reduction potential and light weight can exhibit a very specific capacity and specific energy. The use of Li metal however, brings different safety issues. The high reactivity of lithium leads to the formation of dendrites, which in turn leads to short circuit. Another disadvantage of lithium metal is that at very low voltage, the electrolyte undergoes decomposition, to form a SEI layer, on the surface of lithium electrode which leads to an irreversible capacity loss during the first few cycles. For safety reason graphite is used as anode material, commercially.

The key requirements for anode materials to be successfully used in LIB application are summarised below:

- i) An ideal anode must contain elements or compounds with low atomic or formula weights, have low density, accommodation fairly large amounts of Li^+ per formula unit.
- ii) It should good ionic and electronic conductivity.
- iii) It should not soluble in solvent or electrolytes used in LIB.

Graphite⁴⁵⁻⁴⁷ is commonly used as anode materials today. It has theoretical capacity of 372 mAh/g and practical capacity of about 325 mAh/g.

The list of current status of cathodes and anodes developed today are given in Figure 6

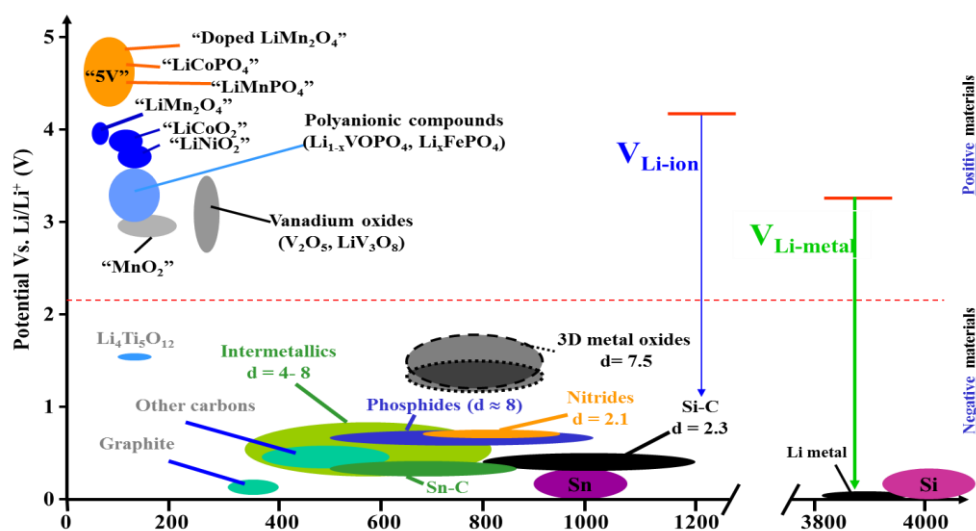


Figure 6: List of current status of cathodes and anodes developed today.

4.4 Electrolytes³²

An electrolyte is a key component of a battery with the electrodes. The electrolytes are generally a lithium metal salt dissolve in organic solvent. The ideal electrolyte for a LIB should full-fill the following criteria:

- i) A high Li-ion conductivity.
- ii) High chemical stability at ambient temperature.
- iii) Its electrochemical stability window should be large so that it can tolerate the high voltage difference between anode and cathode.
- iv) It should able to form solid electrolyte interphase (SEI) at anode if desired.
- v) It should have a high boiling point to provide safety and prevent explosions resulting from high pressure build-up in the cell.
- vi) It should be eco-friendly and inexpensive.

Generally organic based electrolytes like ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonates (DMC) etc. are used as solvents along with lithium containing salts. The Li salts are easily dissolved in these solvents. These have generally oxidation potentials (HOMO) at 4.7 V and reduction potential at about 1 V versus Li/Li⁺. In most of the cases, EC is used as the common solvent because it can form SEI layer very easily upon decomposition of electrolyte. Besides it has highest electrochemical stability voltage window. Generally used Li based salt is LiPF₆. At high temperature of 60⁰C it decomposes to LiF and PF₅. And presence of water can lead to formation of HF, PF₃O and LiOH etc. All these side reaction can lead to degradation of battery performance.

Ionic liquid based electrolyte has been emerged in the recent times. But unfortunately the conductivity of Li-ion is very low because of high viscous nature of ionic liquid.

5. Goal of the current project

1. Studying Li₂CoSiO₄ as a cathode material.
2. Synthesising the material by different syntheses approaches such as Solid State, Polyol and Solvothermal synthesis.
3. Electrochemical performance by galvanostatic charge-discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies.

5.1 Why we want to study $\text{Li}_2\text{CoSiO}_4$?

Recently, $^{29}\text{Li}_2\text{MSiO}_4$ (M= Fe, Mn, Co), as a new group of polyanion compounds, has been recently investigated to meet the high-energy demand in Li-ion batteries. Materials may theoretically allow two-electron exchange per formula unit leading to the double the capacity of currently available cathodes such as LiCoO_2 and LiFePO_4 . During charge/discharge, two-electron exchange can take place, leading to two redox couples $\text{M}^{2+}/\text{M}^{3+}$ and $\text{M}^{3+}/\text{M}^{4+}$ in silicate type cathode material. In case of $\text{Li}_2\text{FeSiO}_4$, $\text{Fe}^{3+}/\text{Fe}^{4+}$ oxidation is not feasible (Fe^{3+} is d^5 system, half-filled orbitals, leads to extra stability). This leads to half of the theoretical capacity of $\text{Li}_2\text{FeSiO}_4$ (166 mAh/g). Because of which $\text{Li}_2\text{FeSiO}_4$ is not of potential interest. Among silicates $\text{Li}_2\text{CoSiO}_4$ has high voltage of 4.5 V and capacity about 325 mAh/g which leads to high energy density of 1463 Wh/kg.

Energy density (maximum achievable) = Specific capacity X voltage

$$= 325 \text{ mAh/g} \times 4.5 \text{ V}$$

$$= 1463 \text{ Wh/kg can be achieved from } \text{Li}_2\text{CoSiO}_4.$$

5.2 The difficulties associated with silicate cathodes:

But practically less capacity and cycle life is achieved because of poor conductivity and structural instability during charge-discharge of silicates. These factors are also leading to poor C rate performance and high irreversible capacity. Because of which silicates are not able make use of practical lithium-ion batteries. Besides electrolyte stability could be an important factor when particularly $\text{Li}_2\text{CoSiO}_4$ is used which operates close to 5V.

5.3 Literature reports on $\text{Li}_2\text{CoSiO}_4$ cathodes:

Lyness et al.⁴¹ show that the three polymorphs of $\text{Li}_2\text{CoSiO}_4$ exhibit electrochemical activity when ball-milled, although with severe capacity fading after a few cycles, which is also the case for the corresponding cobalt-based phosphate, LiCoPO_4 . For the βI polymorph, coating the as-prepared material with carbon switches on electrochemistry without the need for ball-milling and gives superior charge capacity (170 mA h g^{-1} per 1.1 Li per formula unit) and cyclability, compared with the same phase when ball milled with carbon. Only one Li could be extracted up to 4.6 V in agreement with theoretical predictions. Gong et al.⁴⁰ have prepared $\text{Li}_2\text{CoSiO}_4$ by a solution-hydrothermal route, and find reversible lithium extraction/insertion at 4.1 V vs. Li, but limited to 0.46 lithium per formula unit for the

$\text{Li}_2\text{CoSiO}_4/\text{C}$ composite materials, with a reported charge capacity of 234 mA h g^{-1} . Flake like olivine structured $\text{Li}_2\text{CoSiO}_4$ materials prepared by G. A. Nazri⁴³ using hydrothermal synthesis shows capacity of about 250 mAh g^{-1} at 4 V. However, the patent does not report any other electrochemical performance (Cycle life, C rate performances, kinetics, structural stability etc.)

In overall, $\text{Li}_2\text{CoSiO}_4$ materials demonstrate low conductivity, poor stability, cationic disorder or many other drawbacks, and the use of various modification techniques, such as carbon-coating or compositing. Extensive research is needed for silicates to become most promising candidates for use as cathode materials in the next generation of lithium-ion batteries.

Goal of our Research

Our goal is to improve the electrochemical performance of the material by synthesising $\text{Li}_2\text{CoSiO}_4$ in nanoscale, eliminating electrochemically inert additive through electrode architectures. The use of nanoparticles will enable us high C rate performance whereas electrode architecture will improve the electronic conductivity of the material. Besides, electrolyte additives will be used to make superior electrochemical stability. The $\text{Li}_2\text{CoSiO}_4$ materials have been synthesized by various synthetic routes as described below.

5.4 Synthesising the silicate materials in nano-scale

We synthesize the material by different synthetic approaches such as Solid State, Polyol and Solvothermal syntheses and compare their electrochemical performance. Besides our focus is to synthesise the material in nano-scale³⁰ because nanomaterials have several advantages like:

- 1) High rate of Li^+ diffusion: the reduced diffusion path length for Li^+ ions and electron transport compared to micron-sized particles can increase the rate of charging and discharging
- 2) The volume changes caused by Li^+ insertion/de-insertion will be better accommodated by nano-materials compared to bulk materials due to faster stress relaxation and that prolongs the battery cycle life.
- 3) Enhancement of electron transport within the particle.
- 4) Increase in specific surface area of the active material greatly increases the mass specific amount of active material in contact with the electrolyte. This results in a

higher flux of Li-ion transport across the electrode/electrolyte interface and as a result, less impedance in the charge transfers reaction.

5.5 Disadvantages of nanoparticles:

- 1) Synthesis of nanoparticles can be difficult, and dimensions and stoichiometry may be difficult to control.
- 2) Because of high surface area, the possibility of side reaction increases.
- 3) The overall density of nanoparticles is lower than that of micro particles of same composition. This results in a lower volumetric energy density.

But it's worth synthesizing materials in nanoscale and look into electrochemical performances.

Besides the above syntheses approaches our target is to synthesise the material in olivine phases. Because of excellent structural stability has been observed for LiFePO_4 olivine phase which leads to excellent cycling and C rate performance during charge and discharge.

6. Synthesis

X-Ray Diffraction (XRD), Scanning electron microscopy (SEM), Brunauer-Emmet-Teller Surface Area analysis (BET), Thermal gravimetry analysis (TGA) were used for structural and physical characterization of the samples. Electrochemical performances were characterized by galvanostatic charge-discharge, CV, EIS studies.

6.1 Synthesis of $\text{Li}_2\text{CoSiO}_4$

Polyol and solvothermal synthesis of $\text{Li}_2\text{CoSiO}_4$

$\text{Li}_2\text{CoSiO}_4$ have been successfully synthesised by both polyol and solvothermal syntheses process and compared there electrochemical performance. The Polyol method was first developed by Fievet and coworkers³⁸ as a simple route for obtaining colloidal particles of metals and alloys. One of the important points regarding polyol method is that nano-particles can be easily obtained during synthesis. For this method we use a polyol like solvent such as ethylene glycol (EG) as a reaction medium i.e. all the precursor are dissolved into EG and performed the reaction. The EG used act as a chelating agent so that it prevent agglomeration and end up in getting nano particles. The size of the nano particles can be controlled using reaction time and concentration and others factors. Solvothermal method is conducted in an

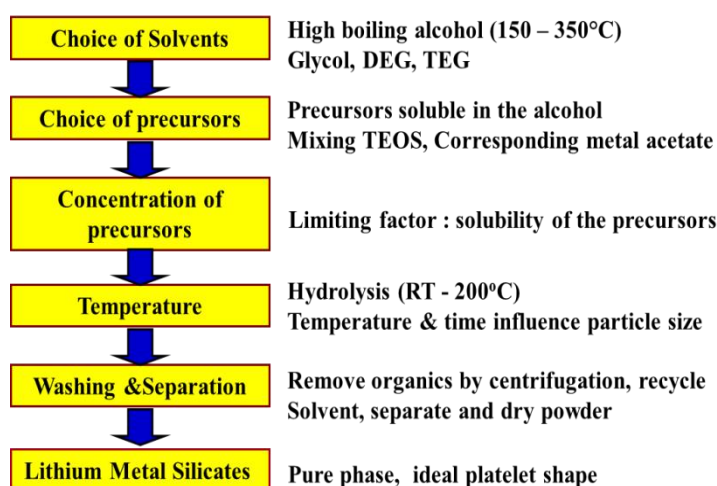
autoclave. Generally an organic solvent like ethanol or methanol or acetone is used as a reaction medium and all the precursors are dissolved in the reaction medium. The mixture is put inside an autoclave and heated at its boiling temperature.

Experimental procedures

All of the reactants were of analytical grade and used without further purification. The chemicals that are used in these experiments are lithium hydroxide monohydrate, lithium acetate monohydrate, cobalt acetate tetra hydrate, tetraethoxy orthosilicate and ethylene glycol as medium for polyol method and methanol solvent medium for solvothermal method.

a) Synthesis of $\text{Li}_2\text{CoSiO}_4$ by polyol method:

Polyol synthesis is one of the successful synthesis approaches to prepare LiMPO_4 compounds. Our goal will be synthesis of nano structured $\text{Li}_2\text{CoSiO}_4$ for better structural stability during charge-discharge process and hence better cyclability could be achieved. For polyol synthesis of $\text{Li}_2\text{CoSiO}_4$ compounds: 2 mol of $\text{LiOOCCH}_3 \cdot 2\text{H}_2\text{O}$ and 1 mol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ are mixed with desired amount of water and dissolved. 4.5 litre/mole of initial precursor of ethylene glycol is transferred into a round bottom flask and the above salt mixture is added slowly into it with constant stirring. 1 mol of TEOS into the solution added from a burette drop wise. The mixture is then refluxed at 196°C for 15 hrs. The resultant product was filtered, washed several times in acetone. The product was dried and pelletized followed by calcination at 700°C for 10 hours under Ar-atmosphere. The schematic of the reaction is given below.

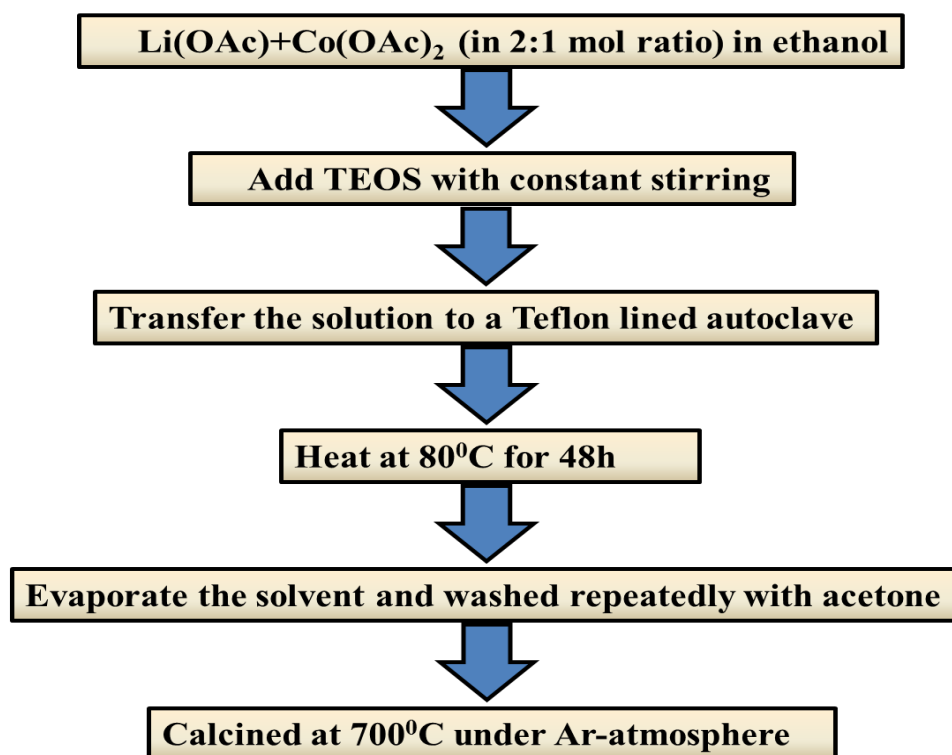


Experimental set-up for polyol synthesis

Schematics of $\text{Li}_2\text{CoSiO}_4$ synthesis by polyol method

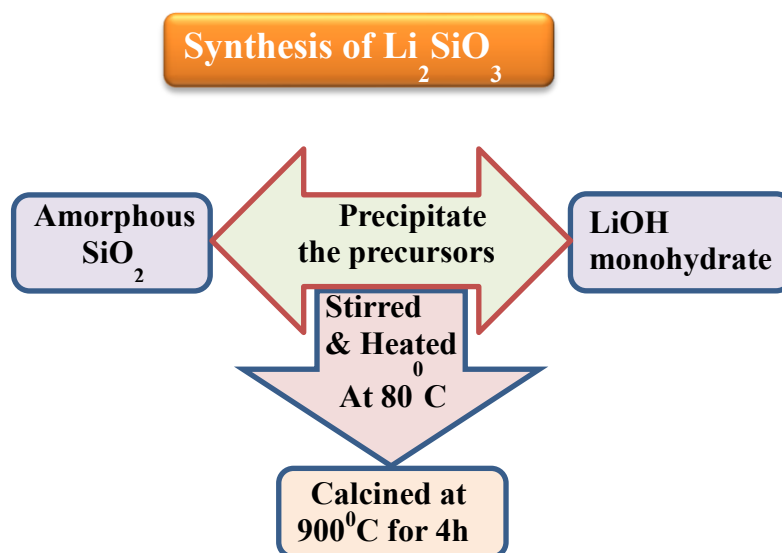
b) Synthesis of $\text{Li}_2\text{CoSiO}_4$ by solvothermal method:

$\text{Li}_2\text{CoSiO}_4$ cathodes will be prepared by solvothermal synthesis which can be brief summarized as follows. 2 mol of $\text{LiOOCCH}_3 \cdot 2\text{H}_2\text{O}$ is mixed with 1 mol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in a mortar and pestle and grind the mixture to fine powders. 1 mol of tetraethyl orthosilicate (TEOS) in ethanol is added in to it. Mix thoroughly and transfer the whole mixture into an autoclave. The reaction mixture is heated at 80°C for 24 h. The desired product is repeatedly washed with ethanol and water in order to remove esters, acids. The mixture is dried under ambient condition and finally calcined at 700°C for 10 hours under argon atmosphere to get the final product.



Schematics of $\text{Li}_2\text{CoSiO}_4$ synthesis by solvothermal method

Besides, $\text{Li}_2\text{CoSiO}_4$ can be obtained from the initial precursors of 1 mol of Li_2SiO_3 and 1 mol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ using the above described synthesis process. The precursor Li_2SiO_3 that is used here has been synthesized by co-precipitation method³⁹.



Synthesis scheme of Li_2SiO_3

6.2 In situ C-coating:

The $\text{Li}_2\text{CoSiO}_4$ pristine material (80%) was mixed with pitch (20%) in N-vinylpyrrolidone and stirred the mixture for 24 hours. The obtained slurry was dried at 90°C followed by heating at 400°C for 6 h under Ar-atmosphere.

7. Structural characterisation

The as prepared pristine samples are crystallized, the materials obtained are amorphous. So pristine samples are heated at 700°C for 6 hrs in inert atmosphere to get the desired crystallized product. Powder XRD was used for structural analysis of the synthesized materials. The XRD patterns of $\text{Li}_2\text{CoSiO}_4$ were obtained using a Panalytical X-pert diffractometer with a Cu $K\alpha$ radiation operated at 40 kV and 30 mA at scan rate of 0.016 between 20 and 70 degrees.

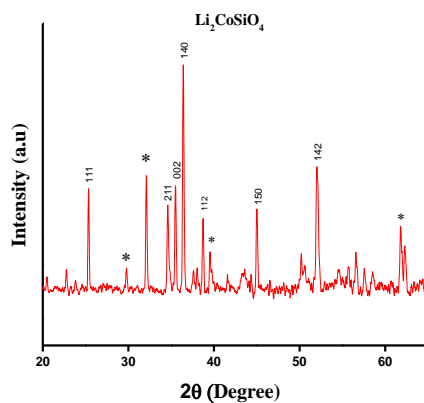


Figure 7: XRD of $\text{Li}_2\text{CoSiO}_4$ prepared by polyol method (Compared with the PDF no.702357)

The XRD pattern of $\text{Li}_2\text{CoSiO}_4$ samples prepared by polyol method is shown in Figure 7. In the pattern four impurity peaks of Co_3O_4 are detected. The crystal system for the sample is found to be orthorhombic, and the space group is $\text{Pbn}2_1$. The corresponding cell parameters are $a=6.253 \text{ \AA}$, $b=10.68 \text{ \AA}$, $c=4.929 \text{ \AA}$ and $\alpha=\beta=\gamma=90^\circ$. By comparing with the PCPDF no. 702357 we have confirmed the structure of $\text{Li}_2\text{CoSiO}_4$.

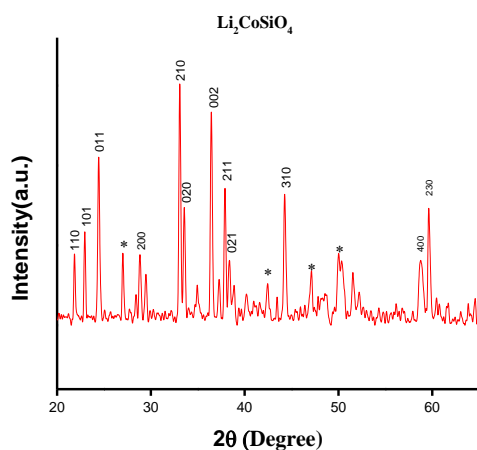


Figure 8: XRD of $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method (Compared with the PDF no.240608)

The XRD pattern of $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method is presented in figure 8. For this synthesis Li_2SiO_3 is used as precursor material, which is also synthesised in laboratory and its XRD is discussed later in this section. XRD pattern of $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method shows some impurity peaks corresponds to Li_2SiO_3 . The crystal system for this system is found to be orthorhombic and the space group is $\text{Pmn}2_1$. The cell parameters are $a=6.28 \text{ \AA}$, $b=5.36 \text{ \AA}$, $c=4.94 \text{ \AA}$ and $\alpha=\beta=\gamma=90^\circ$. The pattern is compared with the PCPDF No. 240608.

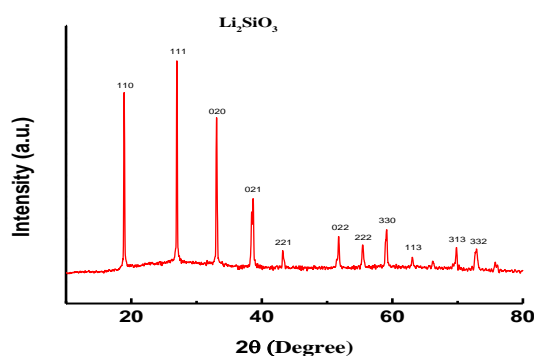


Figure 9: XRD of Li_2SiO_3 prepared by co-precipitation method (Compared with the PCPDF No.240608)

By comparison with the PCPDF No. 240608 we have found that the crystal system for Li_2SiO_3 is also orthorhombic. Phase pure Li_2SiO_3 was obtained.

8. Morphology of $\text{Li}_2\text{CoSiO}_4$

The morphology of $\text{Li}_2\text{CoSiO}_4$ particles are observed with a scanning electron microscope. The SEM images of the $\text{Li}_2\text{CoSiO}_4$ prepared by polyol route and solvothermal route are shown in Figures 10 and 11.

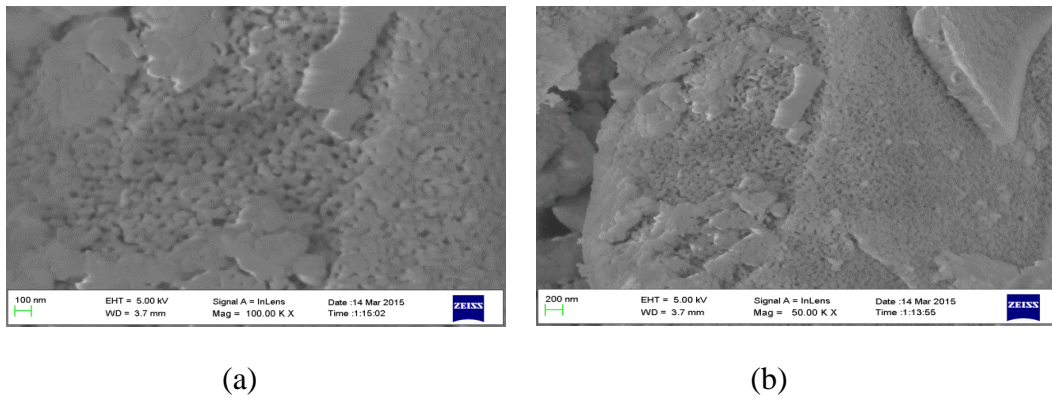


Figure 10: SEM images of $\text{Li}_2\text{CoSiO}_4$ prepared by polyol method.

SEM images of materials synthesized by polyol method at different magnifications shown in Figure 10 indicate that the materials are comprised of large secondary particles and nano-grained primary particles. The primary particles in nano-scale increases Li^+ ion diffusion. At the same time large secondary aggregates helps to reduce side reactions and increases overall tap density (volumetric energy density). Higher magnification image (a) shows the larger secondary particles comprising of primary particles in the range of 30-40 nm.

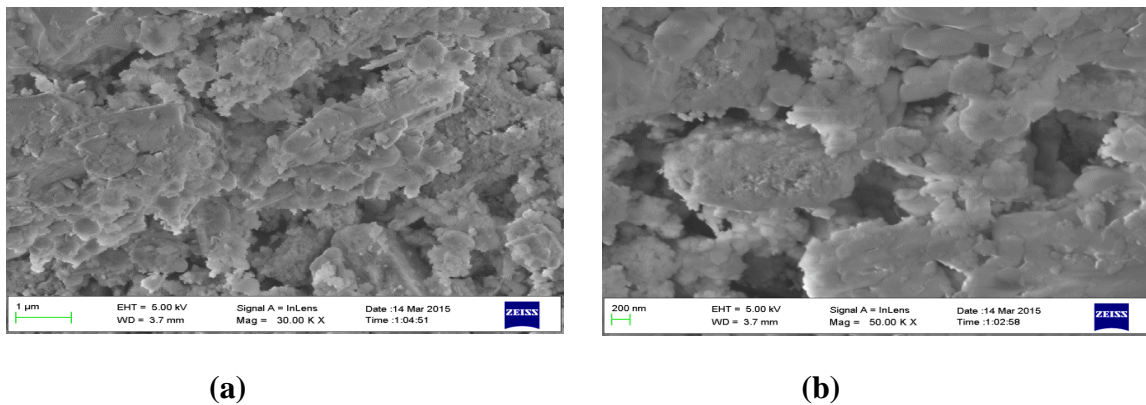


Figure 11: SEM image of $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method

SEM images at different magnification (30K and 50K) of $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method are shown in Figure 11. From these images it's very difficult to predict exact particle size for these materials. However one can predict spherical morphology and average size of the particles are in the range of $0.5\mu\text{m}$ - $1.0\mu\text{m}$ tentatively. A higher magnification (100K) image is desired to see the appropriate size of the particles which is under progress.

9. Electrochemical Study of $\text{Li}_2\text{CoSiO}_4$

Electrode preparation

Electrochemical performance such as galvanostatic charge-discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were studied in 2 electrode type Swagelok or CR2032 coin type cells. The electrodes were prepared by using active material (80%), binder PVDF (polyvinylidene fluoride) (10%) and C-black as conducting additive (10%) in N-Vinyl Pyrrolidone (NVP) to make slurry. The slurry was coated on to an aluminium foil current collector using doctor blade and dried under vacuum for about 12h.

Assembly:

1cm^2 electrodes were punched and used as cathode. Lithium foils were used as anodes and reference electrodes for all electrochemical measurements. Basically, all the electrochemical measurements were conducted in half cells. The cells were assembled using a cathode, lithium foil anode; polyethylene-polypropylene tri-layer separator was sandwiched between them. LiPF_6 (1.0 M) in EC:DMC (1:2) was used as electrolyte. Assembly was done in an argon-filled glove box (M-Braun) having less than 1ppm levels of moisture and oxygen.

Electrochemical cycling

The charge-discharge electrochemical cycling and C rate performance testing were performed at C/50 rate between 2.5V-4.5V using constant current (CC)-constant voltage (CV) protocol. High voltage (up to 5V) electrochemical cycling's are under progress with vinylene carbonate electrolyte additive.

EIS measurements of $\text{Li}_2\text{CoSiO}_4$ composite electrodes were carried out during open-circuit voltage using a battery test unit model 1470E coupled with an FRA model 1455 from Solartron Analytical Ltd., controlled by Z-Plot software from Scribner Associates. EIS

studies were carried out in a 2-electrode configuration using a lithium metal as counter. EIS was carried out in a frequency range between 100 KHz and 10 mHz with 10 points per decade in frequency. For clarity, only few relevant voltages are presented in the figures. EIS are normalized by the geometric area ($\sim 1 \text{ cm}^2$) of the electrode.

Till now literature⁴⁰⁻⁴² results show the high irreversibility of $\text{Li}_2\text{CoSiO}_4$ which could be due to very poor conductivity of $\text{Li}_2\text{CoSiO}_4$ and structural stability. Here we are trying to address the conductivity issue and later we will focus on structural stability. The conductivity of the samples is increased by in-situ C-coating using petroleum-pitch as described above. The electrochemical impedance spectroscopy study shown in figure 12 shows lower solution, Ohmic and Charge transfer resistance for the carbon coated material in relation to the pristine uncoated $\text{Li}_2\text{CoSiO}_4$.

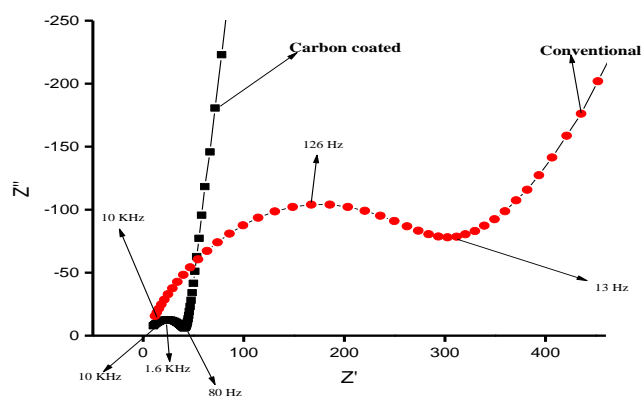


Figure 12: Impedance spectra, represented as Nyquist plots, of $\text{Li}_2\text{CoSiO}_4$ composite electrodes at 25 °C measured at OCV between the frequency range 100 KHz and 10 mHz.

From the EIS plot shown in figure 12, we have calculated the resistance of the material with and without C-coating. The Ohmic resistance (R_o for pristine material= 12.5Ω and R_o for C-coated= 9.23Ω) and charge transfer resistance (R_c pristine material = 353Ω and R_c of C-coated = 41Ω) is lower for C-coated electrode amounting to lower electrode polarization and thus improving conductivity. This signifies in-situ carbon coating increases ionic and electronic conductivity of the material in comparison to non-carbon coated material.

The electrochemical performance was studied with charge-discharge cycling profile of the material synthesized by polyol and solvothermal method. The charge and discharge were conducted at C/50 rate between the voltage range 2.5V-4.5V. Here we report the charge and discharge profile for first two cycles.

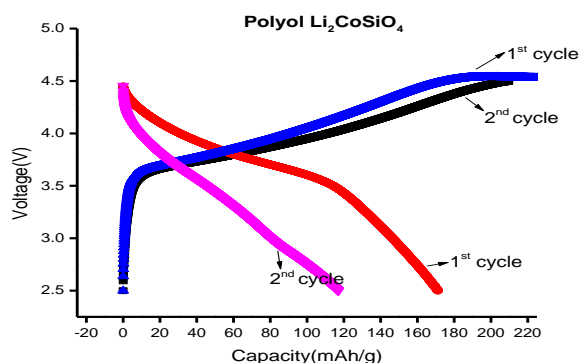


Figure 13: Charge-Discharge voltage profiles of $\text{Li}_2\text{CoSiO}_4$ prepared by polyol method during 1st and 2nd cycles.

We have presented first two cycles because to see irreversible capacity and subsequent capacity loss. The 1st charge cycle the capacity observed around 220 mAh/g, which is equivalent to 1.5 Li-ion extractions at 4.5 V. The first discharge cycle capacity observed is about 170 mAh/g which is very close to 1 electron capacity. Irreversible capacities of these electrodes are in the range about 20%. We expect charging to 5V with electrolyte additive could lead to the full discharge capacity of > 300 mAh/g. The 2nd cycle the charge capacity is approximately 190 mAh/g and discharge capacity is 120 mAh/g. The rapid capacity loss could be due to structural instability and low electron conductivity of uncoated carbon (pristine) samples. So, in 2nd cycle itself a lot of irreversibility is observed. It should be noted here the capacity presented here is much better than the reported.

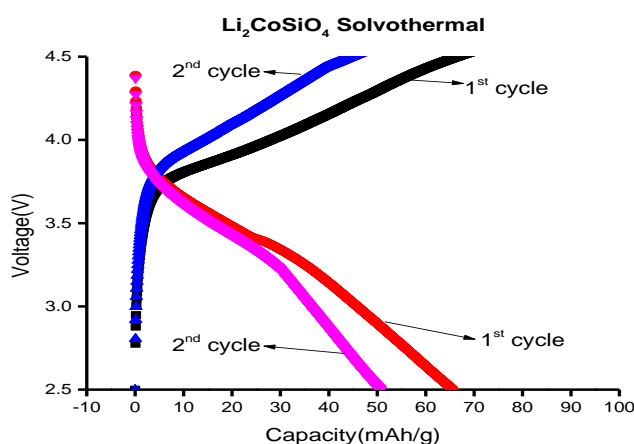


Figure 14: Charge-Discharge profile for $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method during 1st and 2nd cycle.

The Charge-Discharge profile for $\text{Li}_2\text{CoSiO}_4$ prepared by solvothermal method is presented in figure 14. 1st cycle the charge capacity comes around 80 mAh/g and the discharge capacity around 60 mAh/g can be achieved which is much lesser than the material synthesized by polyol method. This could be attributed to the comparatively small particle size of $\text{Li}_2\text{CoSiO}_4$ prepared by polyol method than solvothermal method. So we expect faster diffusion of Li^+ ions in polyol method than solvothermal method.

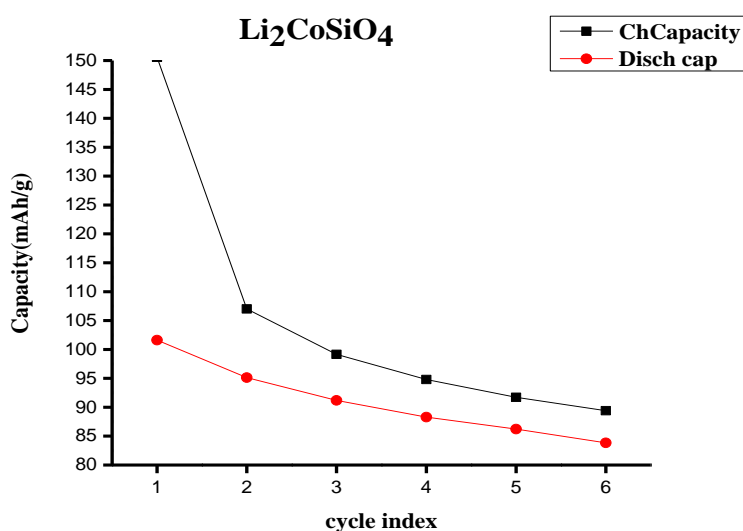


Figure 15: Charge and discharge capacity up to six cycles

So from figure 15, it can be conclude that the capacity fading for $\text{Li}_2\text{CoSiO}_4$ is very much i.e. this material is not so stable.

10. Summary and Future directions

We can summarise our current work briefly as follows.

- ❖ We have successfully synthesised $\text{Li}_2\text{CoSiO}_4$ by polyol method and studied electrochemical performance. The crystal structure of the sample is found to be orthorhombic, and the space group is $\text{Pbn}2_1$. We have achieved more than 1.5 electron capacity. Capacity decay could be attributed to structural stability. These studies are under progress.
- ❖ We too have synthesised $\text{Li}_2\text{CoSiO}_4$ by solvothermal method, by using different precursor material and studied their electrochemical performance. The performance of $\text{Li}_2\text{CoSiO}_4$ synthesized by solvothermal method much lesser than the material synthesized by polyol method. This could be attributed to the comparatively small

particle size of $\text{Li}_2\text{CoSiO}_4$ prepared by polyol method than solvothermal method which leads to faster Li^+ ion diffusion.

- ❖ SEM images clearly identify nano-size particles of the materials. But high resolution images are required to further confirm this.
- ❖ In situ C-coating enhanced the electronic conductivity and expected to have better electrochemical performance which is under progress.

❖ **On-going studies:**

- We are working on structural distortion which occurs during charge and discharge. Our goal is now to synthesise the material in olivine phase.
- 3D electrode architectures to improve further electronic conductivity and hence capacity retention and energy density of silicate cathodes for Li-ion batteries⁴⁴.
- Efforts will be directed for the operation of these materials to high voltage cycling (5V) by using electrolyte additives in order to get 2 electron capacities.
- Cycling studies and other electrochemical studies (CV and EIS are under progress).

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