A Review of Anode Material for Lithium Ion Batteries

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Abstract— In this study an attempt has been made to review the use of anode material for Li ion batteries, with a special focus on Cobalt Ferrite. The review includes a discussion of historical background, review of Cobalt Ferrite and some yesteryear anode materials.
Keywords: Cobalt Ferrite, Lithiation, Delithiation, Morphological properties, structural properties, transition metal oxides.

1. Introduction
As more and more energy sources are getting depleted year by year, the world is craving for newer types of renewable energy sources. The clamour for making mother earth greener is echoing everywhere. Due to the rising CO2 levels, earth is in dire need of cleaner energy sources. Alternative sources are badly needed for countering the ever-threatening increase in pollution levels. Transport vehicles are contributing immensely to the woes. The struggle for replacing the existing fuel items with LIBs will continue. Though they are being used widely, these ecofriendly batteries are facing numerous challenges. The materials for making LIBs, of which the electrode materials are playing a vital role, are increasing the electrochemical performance of the aforementioned.

In the past graphite was the electrode material, especially the anode. But, it had a lot of drawbacks such as a low theoretical capacity of 372mAh/g, low cyclability, poor electro chemical performance and volume strain. The search for suitable anode materials latched on to transition metal oxides, like Cobalt Ferrite, which minimizes the crippling afflictions to an extent. It is also well known for its magnetic hardness with high coercivity. It shows moderate structural stability [61].

With the advent of CFO, things have changed drastically as they are of low cost and of greener background. These are spinel ferrites nanoparticles with general formula AFe2O4 [where A=Mn, Co, Ni, etc.].

CFO has a remarkable chemical stability and mechanical hardness. The Cobalt Ferrite was picked due to its high theoretical capacity of 916mAh/g against the 372mAh/g of graphite [53]. The redox conversion reaction of CFO contributed to lithium storage mechanism. In spite of all its advantages, it suffered from poor electrical conductivity, electrode pulverization, poor cyclic stability and poor rate capability.

The ongoing study aims at furthering the performance of spinel based CoFe2O4. The abrupt volume changes during lithiation / de-lithiation process have to be minimized. To enhance the electrochemical performance of transition metal oxides like CFO, an attempt has been made to use transition metals in it. Studies have proven that this addition makes CFO more electrochemically active. But, not many studies have been made in this regard. The doping of CFO with transition metals like Vanadium and Zirconium is little. This offers better structural stability and high reversible capacity [80].
2. Historical Background

Batteries of the past had a Mesopotamian origin. It was Italian physicist Alessandro Volta who invented the first battery in 1800. He prepared it from stalked discs of Copper and Zinc. In primary batteries the reverse reaction was not possible. It was John Goodenough who brought a new dimension into the manufacture of batteries, when he invented Lithium ion batteries. In this type of batteries Li ions move from one electrode to another. The credit for the popularity of Li ion batteries goes to Sony after the 1990s. Then Goodenough modified Li ion batteries. The working of Li ion batteries depended on their electrodes. So, there was a hunt for suitable anode materials. Search was on for high theoretical capacity, stable crystal structure and high conductivity.

Silicon anodes with high theoretical capacity were used as anodes. They suffered volume expansion, and the materials like titanium oxide and lithium titanate that were used had the peculiarities of low volume expansion with stable crystal structure. But, the theoretical capacities were low. To eliminate the aforementioned problems transition metal oxides have gathered attention.

3. Working of Li ion batteries

The three main components of a battery are anode, which is negative electrode, Electrolyte and cathode, which is positive electrode. The process during the charging is the generation of cations like Li+ or anions like OH-, and their movement across the electrodes. These cations or anions stick on to, or are assimilated by, the electrodes. The Lithium ions reach the cathodes and anodes in either charging or discharging cycles. The electrolyte conducts Li ions between anode and cathode. The generation of electrons in the external circuit is due to the transport of Li+ ions through the electrolyte. During charging and discharging electrons are generated.

The three methods used to make anode in Li ion batteries are intercalation-based method, conversion reaction-based method and alloying reaction-based method. In the intercalation-based method Li ions are electrochemically intercalated into the space between the layers of materials. It has a lot of advantages with high discharge/charge efficiency. The major drawback of this method is the occurrence of some irreversible reactions during the lithiation process, which causes the cathodic decomposition of a number of constituents of the electrolyte. Similarly, if graphite is used, low capacity is a major problem. So, the hunt is on for other carbonaceous materials to obtain a better performance.

The conversion reaction-based materials is for mainly faradic reaction. The theoretical capacity of conversion reaction is remarkably high. The major shortcomings are pulverization and electric isolation. But to improve the volume change, high surface area structures are employed (like mesoporous materials). The alloying reaction-based method consists of making alloys of Silicon, Germanium and Tin with lithium. These alloying reaction-based materials are most famous for their high specific capacity. Reducing volume expansion is the main step here. For this, reducing the size of the metal particle size is an option.

The major anode materials used are

Graphite, nanostructured carbonaceous materials, metal oxides, metal nitrides, metal sulphides, metal phosphides, silicon, Germanium, Tin, Phosphorous, Antomony, Indium, etc.

preparation Techniques

Co-precipitation is a phenomenon, where a solute that would normally remain dissolved in a solution precipitates out on a carrier that forces it to bind together, rather than remain dispersed. Co-precipitation is a process in which the required cations from common medium are co-precipitated, usually as hydroxides, oxalates or titrates. These precipitates are calcined at appropriate temperatures to yield the final powder. Co-precipitation results in atomic scale mixing, and hence the calcining temperature required for the formation of the final product in low, which leads to a low particle size. Also, the precipitation process requires us to control the concentration of the solution PH, temperature and the stirring speed of the mixture in order to obtain the product with the required properties.
Characterization Techniques,

1. The structural analysis, chemical composition and the morphology of the samples can be studied by XRD.
2. Thermal gravimetry analysis.
3. Chemical composition can be investigated by X-ray photoelectron spectroscopy.
4. The morphology and structure samples can be investigated by Field Emission Scanning Electron Microscopy.

A Review of Cobalt ferrite

A review of cobalt ferrite has been carried out for the precise inference quoted by various researchers all over the world including the technique of preparation and characterization.

| Method of preparation of cobalt ferrite | Reference no. | Raw materials and solvent | Characterization technique | Inferences |
|----------------------------------------|---------------|--------------------------|---------------------------|------------|
| Urea assisted auto combustion synthesis | [53]          | Cobalt nitrate, iron nitrate, deionized water and urea | XRD,FE-SEM | The threshold limit of lower stoichiometry in cobalt ferrite that leads to impressive electrochemical performance. |
| Co-precipitation                        | [55]          | FeCl₃·6H₂O CoCl₂·6H₂O Oleic acid Y₂O₃,Tb₂O₇,cetyl trimethyl ammonium bromide, aqueous ammonia, HNO₃, Urea, NaOH, Ethanol, Deionized water  | XRD,TEM,VSM | Peaks from XRD are broad and sharp showing cobalt ferrite in low crystallizatio. The luminescent intensity and luminescence color has changed due to ferromagnetic cobalt ferrite core introduction. |
| Simple hydrothermal method              | [84]          | Ammonium iron sulphate hexa hydrate, cobalt (II) sulphate heptahydrate and Nickel sulphate hexa hydrate, glucose | XRD,SEM,XPS | XRD result shows that all the peak positions have no shifting with Ni doping. |
| Hydrothermal method                     | [67]          | FeCl₃,KNO₃,ZnC₄H₆O₇.4H₂O,CoC₄H₂O₂,2H₂O,acetone | XRD,SEM,HRTEM | At 1694 and 1928mA/g |
| Method                  | Ref. | Materials                                                                 | Characterization Methods | Notes                                                                                                                                                                                                 |
|-------------------------|------|---------------------------------------------------------------------------|---------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Thermal decomposition   | [87] | Cobalt acetate (Co(C₂H₃O₂)₂.4H₂O) Iron Sulphate (Fe(NO₃)₃.9H₂O,Citric acid) | XRD,FESEM,VSM             | For each of the magnetic parameters there is visible size dependency.                                                                                                                                 |
| Sol-gel process         | [37] | Nitrate salts of Co and Nickel, citric acid,                             | XRD,SEM,FT-MIR           | High electrochemical performance was attained for samples annealed at high temperature.                                                                                                                  |
| Co-precipitation        | [80] | CoCl₂ and FeCl₃.6H₂O,Acqueous solution of NaOH                           | XRD,SEM,XPS              | According to result pure spinel structure is formed and active electrochemical performance was found.                                                                                                  |
| Co-precipitation        | [46] | First a solution was prepared by dissolving 5.40 g of active cathode material from LIB in 30ml/L of HNO₃ and H₂O.hexahydrateferric chloride P.A, ammonium hydroxide P.A, ammonium acetate solution. | TGA,XRD,SEM              | XRD confirmed the formation of CoFe₂O₄.Inth e study cobalt was recycled fromspinel lithium ion batteries.                                                                                       |
| Simple hydrothermal method | [95] | Graphene oxide, iron chloride, cobalt acetyl acetonate, ascorbic acid, hydrazine hydrate, ethanol, deionized water, carbon black, polyvinylidene fluoride, N-methyl-Z-pyrrolidene, copper foils | XRD pattern of Goad GS_CFO, Raman spectra, SEM | The prepared nanocomposites used to get the homogenous CFO NPs on the graphene nanosheets.                                                                                                        |
| Mechanochemical method  | [48] | Cathode material For lithium cobalt oxides, LiOH.H₂O and Co(OH)$_2$ For spinel lithium manganese oxide, From(MnO$_2$,Mn$_2$O,MnO) and |                         | The synthesis process was enhanced by mechano-chemical                                                                                                                                         |
| Process / Method                                      | Solution / Reaction / Reagents                                                                 | Analysis Methods / Results                                                                 |
|------------------------------------------------------|-----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Chemical vapour deposition                           | Solution containing iron (III) acetyl acetonate, cobalt acetate, methanol. The film electrodes of cobalt ferrite were deposited by AACVD on to fluorine doped SnO₂. | XRD, Raman spectroscopic analysis and SEM. The formed cobalt ferrite is pseudo-capacitive and highly conducting. |
| Through novel aqueous method                         | An aqueous solution of 0.1 M betaine mixed with 0.1 NaOH,CoCl₂.6H₂O and FeCl₃. H₂O, deionized water, NaOH, ethanol | XRD, HRTEM, SEM, TGA-DSC and EDX. Successfully prepared octahedral shaped cobalt ferrite NPs. |
| Electrophoretic method                               | Pure iodine, Acetone, citric acid, ammonia, ethanol, Fe(NO₃)₃.9H₂O, Co(NO₃).9H₂O, sulphuric acid and nitric acid | XRD, FE-SEM, DLS (Dynamic light scattering analysis). On carbon fibres cobalt ferrite NPs were deposited. |
| Calcining the precursor material                     | CoCl₂.6H₂O, FeCl₂.4H₂O, FeCl₃.6H₂O, NaOH, deionized water, anhydrous ethanol and HNO₃         | XRD, XPS (Oxygen bridge), Raman spectroscopy, HRTEM and EDS. The interfacial interaction had huge impact on product. |
| Reverse micelles method                              | Two different reverse micelles containing aqueous solution of metal chlorides and NaOH solution | XRD, SEM and SPES. It was revealed that huge agglomerates of primary particles were present. This is a suitable method to synthesize anode materials. |
| Controlled hydrothermal synthesis and thermal decompositio n treatment | FeCl₃.6H₂O, CoCl₂.6H₂O, C₆H₈O₆, Co(NH₂)₂, deionized water | XRD, SEM, TEN, and XPS. Cobalt ferrite microsphere show high discharge capacity and good cyclic performance. |
| Calcination and thermal treatment                     | LiCoO₂ was separated from anode material, chemical grade iron oxide was added for the synthesis of ferrite. | XRD and VSM. Coercivity and saturation magnetization values of made Composite enhanced with |
| Method                                      | Reaction Components                                                                 | Characterization Techniques | Notes                                                                 |
|---------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------|----------------------------------------------------------------------|
| Sol-gel synthesis                           | AAO templates, Fe(NO₃)₃.₉H₂O, Co(NO₃)₂.₆H₂O, citric acid, deionized water and ammonia | XRD, FTIR, FESEM, and SAED   | Single phase cobalt ferrite nanowire arrays are synthesized.          |
| Hydrothermal process                        | Ferric (III) nitrate nanohydrate Fe(NO₃)₃.₉H₂O, cobaltic (II) nitrate hexahydrate CO(NO₃)₂.₆H₂O and sodium borohydride NaBH₄ | XRD, Raman spectra, TEM, SEM and XPS | The characterizations revealed formation of GO/SmFe₅O₁₂/CoFe₂O₄ ternary nanocomposites. |
| Microwave assisted combustion method        | Ferric nitrate, cobalt nitrate, anhydrous ethanol and water                         | XRD, SEM, CV and EIS         | Developed a new HRP biosensor based on entrapment on HRD in cobalt ferrite NPs-chitosan nanocomposite for finding out H₂O₂. |
| Water-gas shift reaction                    | Cobalt(II) chloride, Ferrous (II) chloride, deionized water, NaOH and ethanol       | SEM, FE-SEM, EDX, XPS and FTIR | Bimetallic Co-Fe oxide has designed which has more conductivity and transport thereby high charge storage. |
| Sol-gel auto combustion method              | Iron nitrate, cobalt nitrate, citric acid, ammonia, methanol, acetone               | XRD, FE-SEM                 | XRD shows CFO films grown under different working oxygen pressure.    |
| Electro deposition                          | Al foil, ethanol, H₂SO₄, phosphoric acid, chromic acid                               | XRD, FE-SEM and HRTEM       | Having diameters of about 20nm cobalt ferrite-arrays were made.       |
| Template-electro deposition                 | Al foil, ammonia, CoSO₄, H₂O, FeSO₄.₇H₂O                                           | SEM, TEM and XRD            | Successfully prepared cobalt ferrite                                 |
| method                          | formula/ingredients                                                                 | techniques                                      | nanowire arrays with AAO templates |
|--------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------------|--------------------------------------|
| Sol-gel template approach      | Pure salt (MTX), graphite, H$_3$PO$_4$, NaOH, K$_2$S$_2$O$_3$, P$_2$O$_5$, KMnO$_4$, Ammonium hydroxide, Co(NO$_3$)$_3$, H$_2$O, Fe(NO$_3$)$_3$, 9H$_2$O, NaBH$_4$, 1-hexylionic-3-methylimidazolium hexafluorophosphate | SEM, TEM, XRD, FTIR, and cyclic voltammogram     | Ordered cobalt ferrite nanowires with diameter 100 nm has been successfully fabricated. |
| [94]                           |                                                                                      |                                                 |                                      |
| Solvothermal method            | Cobalt nitrate, iron nitrate, citric acid, ethylene glycol.                           | XRD, E-SEM, TEM and VSM                        | Cobalt ferrite-G nanocomposite as MSPE adsorbent coupled with suitable detection techniques will be convenient reliable for analysis of trace SAs. |
| [14]                           | graphite powder, H$_2$O$_2$, H$_2$SO$_4$, FeCl$_3$, 6H$_2$O, CoCl$_2$, 6H$_2$O, KMNO$_4$, sodium nitrate. | SEM, FT-IR, XRD and VSM                        |                                      |
| [41]                           |                                                                                      |                                                 |                                      |
| Electro catalysis              | Pyridine, benzene, H-ncc, unhydrogen ethanol, iron nitrate nonhydrate, cobalt nitrate hexa hydrate | XRD, SEM, TEM                                  | Spinel cobalt ferrite NPs were successfully immobilized as hNCCNC. |
| [17]                           | Cobalt, nickel, manganese and iron single oxides                                     | XRD, cyclic voltammogram and SEM.               | The oxide powders are stable with partial replacement of Fe by Ni and Mn in cobalt ferrite brings electrodes with high surface area. |
| Thermal                        | PVA,                                                                                 | XRD, TEM, SEM and                               |                                      |
| [25]                           |                                                                                      |                                                 |                                      |
| Technique                          | Reagents                                                                 | Characterizations                                                                 | Additional Information                                                                 |
|-----------------------------------|--------------------------------------------------------------------------|-----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Decomposition                     | H₂C₂O₄, FeSO₄·7H₂O, Distilled water, CoSO₄·6H₂O                           | FT-IR                                                                            | Precursor and cobalt ferrite superstructures have been showed to have catalytic activity. |
| Electrochemical oxidation         | CoSO₄·7H₂O, FeSO₄·7H₂O, KOH, Copper and Titanium and fluorine doped in tin oxide, HCl | Atomic absorption spectroscopy                                                     | Cobalt ferrite thin films have been successfully deposited on various conducting substrates |
| Vacuum arc evaporation            | Molybdenum rod, cobalt ferrite cylinder, α-Fe₂O₃, SiO₂/Si.               | XRD, VSM                                                                         | The resultant product showed strong in place anisotropy.                                 |
| Pulsed–laser deposition technique | Cobalt ferrite thin film were deposited on Si with a PLD system.         | XRD, VSM, AFM, TEM                                                               | Oxygen ions in the films increase exchange interaction between magnetic ions.            |
| Sol-gel template method           | Aluminium foil, H₂SO₄, Ammonia, H₃PO₄, CuSO₄, FeCl₃, Co(OAc)₂             | XRD, TEM                                                                         | Samples do not any preferential magnetic orientation                                      |
| Solvothermal method               | FeCl₃·6H₂O, CoCl₂·6H₂O, Aniline, Ammonium persulfate, Ethylene alcohol, Ammonia. | XRD, IR, FT-IR, TEM, TG                                                         | Fabricated PANI-CF with cobalt ferrite component                                        |
| Hydrothermal process              | Ferric chloride, cobalt chloride, ethanol.                               | FE-SEM, XPS                                                                       | Unique microstructures of cobalt ferrite synthesized                                    |
| Sol-gel template method           | Fe(NO₃)₃, Co(NO₃)₂, Distilled water ammonia, HgCl₂ solution              | TEM, select area electron diffraction(SAED)                                       | Nanotubes are roughly parallel to each other orderly and uniformly                      |
| Method                                      | Reference | Materials                                                                                          | Techniques       | Notes                                                                 |
|--------------------------------------------|-----------|----------------------------------------------------------------------------------------------------|------------------|----------------------------------------------------------------------|
| Micro wave assisted combustion method      | [81]      | Ferric nitrate, cobalt nitrate, urea (fuel)                                                        | XRD, SEM, CV, EIS| A new hydrogen peroxide based on HRP immobilized into cobalt ferrite – chitosan has been prepared. |
| Electrophoretic deposition                 | [93]      | Cobalt ferrite, diethyl glycol, ethanol, TiO2, alkyl phosphate, Ester, zirconia spheres.          | EDXS, SEM, XRB   | Ferroelectric bilayers were produced.                                |
| Simple chemical reduction method           | [45]      | Aniline, KOH, Ammonium, persulfate, graphene oxide, KMnO4, ethanol, water.                        | XRD, HR-SEM, FT-IR| Novel catalysts of reduced graphene oxide with polyaniline and cobalt ferrite has prepared. |
| Electrospinning method (sol-gel)           | [73]      | Polyacrylonitrile, Poly(methy1methacrylate), Cobalt acetylacetonate, ferric acetylacetonate, N,N-dimethyl formaldehyde. | SEM, TEM, XRD, GA LVANOSTATIC CYCLING | The unique structure of cobalt ferrite with carbon improves the electrochemical performance. |
| Hydrothermal                              | [35]      | oleic acid, Co(NO_3)_2·6H_2O, FeCl_3·4H_2O, Urea, Ammonia.                                      | XRD, FESEM, TEM, XPS | The concentration of oleic acid affects morphology of cobalt ferrite. |
| PLD method                                 | [10]      | Metallic cobalt powder, iron powder, platinum, DMC, ethylene carbonate.                           | XRD, SEM, XPS    | The spinel cobalt ferrite exhibited polycrystalline cubic structure. |
| Electrosprining technique                  | [67]      | Acetic acid, methyl alchohol, iron (III) Nitrate nonhydrate, cobaltous acetate, Tetra acetate.     | XRD, SEM, TGA, XP S, ICP-AES | Showed high specific area                                          |
| Co-precipitation                           | [27]      | FeCl_3·6H_2O, CoCl_2·6H_2O.                                                                     | XRD, TEM          | The magnetic hysteresys                                              |
| Method                                                                 | Compounds                                                                                     | Techniques                          | Comments                                           |
|------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------------|---------------------------------------------------|
| Hydrothermal method [39]                                                | FeCl$_3$.6H$_2$O, CoCl$_2$.6H$_2$O, Acetone, Ethanol, Isopropanol, Diethylene glycol, Acetyl acetone, NaOH | EDX, TEM, FE-SEM, HRTEM             | Increased absorption in both uv and visible region was observed for cobalt ferrite-sensitized TiO$_2$. |
| Electrophoretic deposition (sol-gel and chemical co-precipitation) [91]| Ba(CH$_3$COO)$_2$.3H$_2$O, Ti(C$_4$H$_9$)O$_4$, FeCl$_3$.6H$_2$O, CoCl$_2$.6H$_2$O, NaOH          | XRD, TEM                            | The obtained bilayer had a dense structure with no phase diffusion. |
| Thermal decomposition [25]                                             | FeSO$_4$, COSO$_4$, Ethylene Glycol.                                                           | TEM, HRTEM, VSM, DTA, TG            | Saturation magnetization increases with increasing calcination temperature. |
| Conventional ceramic method [7]                                        | CO$_3$O$_4$, Fe$_2$O$_3$, Nb$_2$O$_5$                                                        | XRD, SEM, FEG-SEM, EDS             | Nb was not taken in to spinel structure to any significant degree. |
| Alkaline co-precipitation followed by hydrothermal decomposition [18]  | Cobalt hydroxide, iron Hydroxide, Toluene, PMMA, NaOH                                         | SEM                                | Magnetic phoretic deposition of functionalized cobalt ferrite NPs in AAO template. |
| Electrospinning (sol-gel) [30]                                         | Co(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.3H$_2$O, Citric acid, N, N-Dimethyl Formamide, Tetrahydrofuran. | SEM, FT-IR, XRD, EXAFS             | The obtained structure changed from amorphous structure to crystalline on increasing calcination temperature. |
| Electrospinning technique and subsequent annealing [67]               | Polyvinylpyrrolidone (PVP), N, N-Dimethyl Formamide, iron (III)acetylacetonate, Co(NO$_3$)$_2$.6H$_2$O. | SEM, TEM, XPS                       | Showed improved electrochemical performance. |
4. Results and Discussion

Research and development of Cobalt Ferrite-based anode material for the Li ion batteries provide us with the knowledge of their electrochemical, structural and morphological properties. Rechargeable lithium ion batteries have wide applications in portable electronic market. They have high energy density and high specific capacities. As most of the transition metals suffer poor electronic conduction, they need to be modified. The surface area of nanostructured electrode materials raises the risk of secondary reactions involving electrolytic decomposition between electrode and electrolyte. Anode materials with both theoretical capacity and a relatively stable structure are urgently required.

5. Conclusion

The paper includes the importance and the prospects of anode materials for lithium ion batteries in the present era. It contains the history behind the advent of Li–ion batteries. The various materials required and the techniques also assume importance. The paper delineates the techniques employed to study the structural, morphological and electrochemical properties.

6. Compliance with Ethical Standards

Conflict of interest: the authors declare that they have no conflict of interest.

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