CHAPTER II

EXPERIMENTAL
2.1 Experimental Procedures

The methods of synthesis, characterization techniques and the theory involved in the cathode material preparation routes are dealt in this section. In general, the materials synthesis methodology can be broadly classified into solid-state, wet-chemical (solution) and vapor phase synthesis.

2.1.1 Solid-State Method

Solid-state route, otherwise known as “beat & heat or shake & bake” method, has gained wide recognition as a standard method for synthesizing ceramic materials. In this method, reactions occur with the chemical adsorption of two components when they come into contact, and then start diffusing towards the inside of the particles. Various elementary reactions proceed parallel to each other in microscopically different areas. This is the reaction why compounds with different mixing ratios of reactions often result in products containing residual oxides as impurities [258].

In solid–state method, respective hydroxides, carbonates or oxides are ground well initially to get a homogeneous mixture of the reactants. Volatile liquids like acetone or ethyl methyl ketone or ethyl alcohol may be used as a medium for homogenization. The intimately mixed powders will then be fired to temperatures, mostly above 800°C for prolonged hours as per requirement. This type of continuous heating requires a number of intermittent grindings to ensure homogeneity and stoichiometry in the final product. Though the solid-state method gives products over 95% yield, it is seldom stoichiometric...
and often contaminated with impure phases. Also due to the prolonged heat treatments at high temperature, loss of any volatile components will also be observed. Besides this, the very same method has led to the search for other facile synthesis approaches like wet-chemical synthesis routes, in view of phase in–homogeneity, particle agglomeration in the final oxide materials and the requirement of higher heat treating time & temperature.

2.1.2 Wet – Chemical Methods

There are varieties of wet-chemical methods for synthesizing materials of interest. Some of them are explained in the subsequent passages.

2.1.2.1 Solid Solution Precursor Method

Some novel chemical methods of preparing solids have emerged recently, which generally involve the application of low temperature and often give high-surface area products. Noteworthy of these is the solid solution precursor method involving the formation of a solid solution between two or more cations in the proper ratio, having an anion lattice that can be modified. Since the cations are already mixed on an atomic scale (hardly 1nm apart) in a single – phase precursor, decomposition, oxidation or reduction is rapid and complete even at low temperatures. This method allows continuous variation of cation composition and hence it is popularly known as solid solution method.
Carbonate or hydroxide solid solution precursor is the most preferred one for the synthesis of monoxide solid solutions of rock-salt structure. The monoxide solid solutions can also be used as the precursors for preparing spinels and other complex oxides. Besides monoxide solid solution, a number of ternary and quaternary oxides of novel structures have also been synthesized by decomposing carbonate precursors containing different cations in the required proportions. Typical case is the synthesis of Ca$_2$Fe$_2$O$_5$ and CaFe$_2$O$_4$ by heating the corresponding Ca$_2$Fe$_{2-x}$Mn$_x$(CO$_3$)$_4$ precursor.

A number of ternary and quaternary metal oxides of perovskite and related structures can be prepared by employing hydroxide, nitrate and cyanide solid solution precursor as well. For e.g., mixed oxides have been synthesized by heat treating the solid solution precursors of the general formula Ln$_{1-x}$M$_x$(OH)$_3$ and La$_{1-x}$M$_x$'M'' (CO$_3$)$_3$ (where Ln= La or Nd and M= Al, Cr, Fe, Co or Ni) in air at 1070K and 1270K respectively for about 1h. Ca$_2$Fe$_2$O$_5$ having a defective perovskite (millerite) structure has several industrial applications and has been processed by solid solution precursor method.

Organometallic precursors are used in the synthesis of a variety of semi conducting materials and super conducting cuprates. In this context, organo aluminium silicate precursors have been used for the synthesis of aluminosilicates [259], while polymeric methyl silylamines have been used to synthesize SiC-Si$_3$N$_4$ fibers [260]. Similarly, silicon nitride has also been synthesized using organometallic precursors.
Other wet chemical routes like spray drying, freeze drying, etc., are also employed to prepare ceramic powders having sub-micron size and narrow distribution of particles without any agglomeration. However, these methods, usually involve longer processing time, costly chemicals and sophisticated equipments, besides requires high temperature of operation. Hence, in recent years there has been a constant interest in identifying some other alternatives to the wet-chemical methods.

2.1.2.2 Co-Precipitation Method

Co-precipitation is an excellent choice when higher purity and better stoichiometric control are required. However, co-precipitation can produce wide particle size distribution with mean sizes ranging from sub-micro to tens of microns, if necessary precautions are taken. Calcination temperatures are usually lower for co-precipitation than any other method. Formation of co-precipitated powder is generally more tedious because of slow precipitation process and sometimes, rigorous washing steps increase the synthesis time [261].

Chemicals like NH₄OH, oxalic acid, etc., which forms dense and insoluble precipitates with the cations of interest are used to precipitate the metal ions as hydroxides or oxalates respectively. If one desires to prepare multi-component systems, the precipitates formed from the precipitant should be of comparable solubility, so that co-precipitation will be homogeneous and the final products will be of the expected stoichiometry. The precipitates are subsequently subjected to heat treatments to get the final compounds. Co-precipitation method is usually adopted for producing oxides.
2.1.2.3 Solution Combustion Method

Many attempts have been made to use the heat generated by exothermic chemical reactions during the synthesis of ceramic materials [262]. This process, popularly known as self-propagating high-temperature synthesis (SPHTS), is also known as furnace less or fireless synthesis or combustion synthesis (CS). In recent years, CS technique has attracted a good deal of attention due to the production of homogeneous, un-agglomerated multi-component ceramic powders without requiring any intermediate decomposition and/ or post Calcination steps [263].

In order for the combustion process to occur, one has to ensure that the initial mixture of the reactants possess high chemical energy. For example, one may add a fuel and an oxidizer when preparing oxides by the combustion method, both these additives being removed during combustion to yield only the product or its precursor [264]. In CS technique, an aqueous solution containing the corresponding metal nitrates (oxidizers) and a suitable organic fuel (reducer), taken in stoichiometric ratio, is allowed to boil, till the mixture is ignited and thus resulting in self-sustaining fast combustion reaction, which produces fine crystalline oxide powders. Even if the desired product is not formed immediately after combustion, the fine particulate nature of the product facilitates its formation on further heating. In certain cases, firing at a higher temperature may be necessary to achieve the expected phase formation. In the above process, the energy released from the exothermic reaction between the nitrates and the fuel, which is usually ignited at a temperature much lower than the actual phase transformation temperature,
can rapidly heat the system to a high temperature and sustain it long enough, even in the absence of an external heat source. Urea is a well-known example of a fuel of the above mentioned category used in the synthesis of a variety of ceramics. The combustion flame temperature has been estimated to be around 1200º C [265] and such an exothermic reaction due to the combustion of urea is responsible for the shorter synthesis time.

2.1.2.4 Microwave – Assisted Method

The applications of microwaves are known quite long back, especially in the field of communication and food processing. The utility of microwaves for synthesizing organic as well as inorganic materials is fairly recent and since then so many organic polymers, condensation products, oxides, silicides, borides etc., have been prepared by using modified or unmodified kitchen microwave ovens [266].

It is well known that the high penetration depths of microwaves and its coupling with lossy materials (microwave active materials) results in a rapid and uniform heating of the entire bulk of the reacting substance [267]. This minimizes the thermal gradients and thereby reduces the time required for particle diffusion and hence the product could be obtained in a relatively short span of time. Consequently, sintering of ceramics using microwaves has been found to be advantages in terms of reduction in sintering temperature and firing time (~ 3 – 30 min). But the application of microwaves to synthesize inorganic materials is limited due to the restricted number of lossy materials.

Nevertheless, literature of recent years show that microwave processing could be a viable route for the synthesis of many inorganic materials [268, 269], sintering of advanced materials and chemical analysis. For instance, doped ZnS phosphor [270], nano CdSe,
PbSe semiconductors [271] and LaCrO$_3$ –electrode / interconnector for SOFC [272] are certain technologically important materials synthesized by microwave processing.

### 2.1.2.5 Hydrothermal Method

Hydrothermal processing encompasses a broad set of technologies, which share a range of operating temperatures and pressures, requiring the usage of engineered pressure systems like autoclaves. This approach has been found to be effective in the direct synthesis of crystalline ceramics from solution. Thus, this process not only avoids the undesired Calcination processes, but also reduces many factors that include particle size ($< 1\mu$) of the final products, synthesis temperature and time significantly. Accordingly, the hydrothermal process makes possible the formation of nano-scale ceramics. Moreover, the products are often obtained in a well-defined form related to stoichiometry, crystal structure & habit and purity, despite the nature of the source materials chosen. A combination of pressure leaching and precipitation cycles can result in the conversion of even a low-grade ore or an inorganic waste material to a commercially valuable product [273].

Most hydrothermal synthesis processes are carried out in Teflon-lined autoclave at moderate temperature ranging from 150-300 °C and preferably at the corresponding solution vapour pressure. A feed slurry or solution consisting of oxides, hydroxides and salts of the corresponding metal oxide product is pumped in to an autoclave, which heats the slurry to the desired temperature. At that temperature, the feed materials react and / or transform primarily through dissolution and precipitation to the stable oxide form. The products thus obtained can be recovered by filtration after cooling the same. A serious of
wash steps may be required to remove any salts that are formed as by-products.” Wet oxidation” is the term used to describe the above process, which is carried out at temperatures below the critical temperature of water (374º C). By this technology, zeolities, electronic ceramics, silicates, pigments etc., have been produced.

### 2.1.2.6 Sol-gel Method

The sol–gel method is the most promising synthesising method since they have many advantages viz., homogeneous mixing at the atomic or molecular level compared to the conventional solid-state method, good stiochiometric control, low synthesis temperature, short-heating time, good crystallinity, uniform particle size and small diameter, even down to nanometer level. The beginning of the sol–gel methods can be dated back to as early as 1846 when J.J. Ebelein discovered the formation of SiO₂ gel by hydrolyzing Si(OEt)₄ [274]. It is a multi-step process involving both chemical and physical processes such as hydrolysis, polymerization, drying and densification. The name “sol-gel” is given to the process, because a distinctive increase in viscosity in the reacting mixture is observed at the stage of gel formation. After the commercialization of lithium secondary batteries in the early 1990s, sol–gel methods were employed to prepare materials for this energy conversion and storage system. Cathode materials mainly include lithium cobalt oxides (LiCoO₂), lithium nickel oxides (LiNiO₂), spinel lithium manganese oxides (LiMn₂O₄), layered LiMnO₂, vanadium oxides and ferrous phosphate. [274] The basic processing steps of this method is shown in the Fig. 2.1
Fig.2.1 The general procedure of sol-gel synthesis
In order to circumvent the Jahn–Teller effect, the introduction of heteroatoms, e.g., Li, Al, Ti, V, Cr, Fe, Co and Ni via sol–gel methods is a preferable option. Perhaps they are similar to those doped by other methods, i.e., enhancing the average oxidation state of manganese, impeding Jahn–Teller distortion and consequent improving of cycling [275]. LiMxMn2-xO4 (M = Cr, Co, Ni, Fe, Ti, Cu, and Zn.) and multi-doped LiMn2O4 spinels are prepared by a sol–gel method. The cation doping can result in an improvement in cycling accompanying a decrease in reversible capacity. The improvement in cycling performance is mainly attributed to the suppression of Jahn–Teller distortion and cation disordering in the multi-doped spinels. The sol–gel method is widely used in ceramic technology[276,277] and more specifically, in the last five years, three peculiar types of cuprate superconductors viz., YBa2Cu3O7, YBa2Cu4O8, and Bi2CaSr2Cu2O7 have been prepared by sol-gel method [278].

2.2 Characterisation of Prepared Cathode Material

The synthesised samples are subjected to physical characterisation such as TG-DTA (thermo gravimetric differential thermal analysis), XRD (X-ray diffraction), SEM (scanning electron microscopy), FT-IR (Fourier Transform Infra Red Spectroscopy), XPS (X-ray Photon-emission Spectroscopy) and then the electrochemical studies were carried out.
2.3 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

2.3.1 Thermogravimetric Analysis (TG)

In this technique the change in sample weight is measured while the sample is heated at a constant rate (or at constant temperature), under air (oxidative) or nitrogen (inert) atmosphere. This technique is effective for quantitative analysis of thermal reactions that are accompanied by mass changes, such as evaporation, decomposition, gas absorption, desorption and dehydration. The micro-balance plays a significant role, during measurement the change in sample mass affects the equilibrium of the balance. This imbalance is fed back to a force coil, which generates additional electromagnetic force to recover equilibrium. The amount of additional electromagnetic force is proportional to the mass change. The thermal events of the sample can be obtained from this analysis.

2.3.2 Differential Thermal Analysis (DTA)

This technique measures the temperature difference between a sample and a reference material as a function of temperature as they are heated or cooled or kept at a constant temperature (isothermal). Here the sample and reference material are simultaneously heated or cooled at a constant rate. Reaction or transition temperatures are then measured as a function of the temperature difference between the sample and reference. It provides vital information of the materials regarding their endothermic and exothermic behaviour at high temperatures.
2.4 X-ray Diffraction (XRD)

X-ray diffraction is an analytical technique used for examine crystalline solids. The powder diffractometers are used for phase identification and quantitative phase analysis. X-rays are electromagnetic radiation with wavelength about $1 \, \text{Å}$ ($10^{-10} \, \text{m}$). These rays are generated by bombarding matter with high energy electrons or x-ray photons. The operative equation for x-ray diffraction is the bragg’s equation $2d \sin \theta = n\lambda$.

In this technique the primary X-rays are made to fall on the sample substance under study. Because of its wave nature, like light waves, it gets diffracted to a certain angle. This angle of diffraction, which differs from that of the incident beam, will give the information regarding the crystal nature of the substance. The wavelength of the X-rays can be varied for the application by using a grating plate.

2.5 Scanning Electron Microscopy (SEM)

In this technique, an electron beam is focused onto the sample surface kept in a vacuum by electric-magnetic lenses (since electron possesses dual nature with properties of both particle and a wave an electron beam can be focused or condensed like an ordinary light). The beam is then scanned over the surface of the sample. The scattered electron from the sample is then fed to the detector and then to a cathode ray tube through an amplifier, where the images are formed, which gives the information on the surface of the sample. The SEM was carried out by the bombardment of electrons of 30 keV on target sample.
particle which was spread earlier over an aluminum stub with the help of a doubled edged tape followed by coating the surface with gold film. Electrons that are emitted from the specimen with energy of less than 50 eV are defined as secondary electrons and are used for specimen investigation. Other than scanning electron microscopic investigation, instrument also imparts the detection of scattered X-ray for the characteristic radiation of a specific element in an energy dispersive system to identify the element.

2.6 Fourier Transform Infrared Spectroscopy (FT-IR)

It involves the absorption of electromagnetic radiation in the infrared region of the spectrum which results in changes in the vibrational energy of molecule. Since, usually all molecules will be having vibrations in the form of stretching, bending etc., the absorbed energy will be utilized in changing the energy levels associated with them. In this technique a single beam of un-dispersed light is passed through the sample and the absorbances at all wavelengths are received at the detector simultaneously. A computerized mathematical manipulation (known as “Fourier Transform”) is performed on this data, to obtain absorption data for each and every wavelength. It finds extensive use in the identification and structural analysis of organic compounds, natural products, polymers, etc.
2.7 XPS (X-ray Photon-emission Spectroscopy)

When a primary X-ray beam of precisely known energy impinges on sample atoms, inner shell electrons are ejected and the energy of the ejected electrons gives the binding energy of the electron to atom. Since, this binding energy of the emitted electron depends on the energy of the electronic orbit and the element it can be used to identify the element involved. Further, the chemical form or environment of the atom affects the binding energy to a considerable extent to give rise to some chemical shift, which can be used to identify the valence state of the atom and its exact chemical form.

An associated process with this method is that when the electron is ejected from the inner orbital a vacancy is left with. Hence, another electron from the outer orbits may fall to fill the vacancy and by doing so emits X-ray fluorescence. The energy of this X-ray fluorescence is sometimes transferred to a second electron (Auger electron) make it to be ejected. Based on the chemical shifts, the chemical environment around the atoms can also be estimated. This measurement is useful determining the valence states of the atoms present in various moieties in a sample. The intensity of ESCA lines of each element used for quantitative measurements.

2.8 Cell Fabrication and Electrochemical Studies

The electrochemical cell was a typical 2016 coin cell (Hohsen Co., Japan) assembled in an argon filled glove box (MBraun, Germany) using lithium foil as anode, Celgard 2400
as separator and 1M solution of LiPF$_6$ in 50:50 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) as electrolyte. The cathode was prepared by a slurry coating procedure. The cathode slurry consisted of 85% of the synthesized material, 10% conducting carbon and 5% poly vinylidene fluoride (PVdF) binder dissolved in n-methyl-2-pyrrolidone (NMP). The slurry was coated over aluminium foil and vacuum dried at 110$^\circ$C for 2 h. The dried coating was pressed under 10 tonnes load for 2 min and blanks (diameter 18mm) were punched out and used as cathode. The coin cells were cycled at a constant current of C/10 rate between 3 to 5V in a battery cycling unit.

2.9 Chemicals and Reagents

Metal sources for the cathode raw materials were from lithium nitrate LiNO$_3$ (99+ %, Acros Organic); manganese nitrate, Mn(NO$_3$)$_2$.6H$_2$O (GR grade Acros Organic); lithium acetate, Li(CH$_3$COO).4H$_2$O (99 %, Lancaster); manganese acetate, Mn(COO CH$_3$)$_2$.4H$_2$O (99.5% Alfa aesar); cobalt nitrate, Co(NO$_3$)$_2$.6H$_2$O (98+%, Merck); chromium nitrate, Cr(NO$_3$)$_3$.9H$_2$O (97+ %, Alfa aesar); nickel nitrate Ni(NO$_3$)$_2$.6H$_2$O (97+%, Merck); ferric nitrate Fe(NO$_3$)$_3$.9H$_2$O (98+%, Alfa aesar); nickel acetate Ni(CH$_3$COO)$_2$.4H$_2$O (98+, Lancaster); cobalt acetate Co(COO CH$_3$)$_2$.4H$_2$O ( 99% Merck); chromium acetate Cr(COO CH$_3$)$_3$ (98+, Lancaster). The reagents used as organic carriers (chelating agents) were glycine NH$_2$CH$_2$(COOH) (98% Acros Organic); maleic acid C$_2$H$_2$(COOH)$_2$ (98%, Merck); oxalic acid (COOH)$_2$.2H$_2$O (99%, Ranbaxy); acetic acid CH$_3$COOH (99.8%, SD finechemicals); Ammonia solution (25 %, Merck) used as pH controlling agent. The electrolyte used Lithium hexafluorophosphate, LiPF$_6$
ethylene carbonate C₃H₄O₃ dimethyl carbonate, C₃H₆O₃ (GR PuriEL, TechnoSemiChem Ltd., Japan) and polyvinylidene fluoride, (-CH₂CF₂-) n (Alfa aesar) NMP (99.5% Sigma ALRich) were used to fabricate the cathode and cell.

2.10 Instruments

The instruments used to prepare and characterize cathode raw materials, cathode and cell were muffle furnace (Indfur furnace; SL R199); Thermogravimetric/Differential Thermal Analyzer (PL Thermal Sciences Instrument, model STA 1500); Scanning Electron Microscope (SEM) (SEM, Hitachi S-3000 H); X-ray Diffraction (XRD), (JEOL 8030 X-ray diffractometer) with nickel filtered Cu-Kα radiation); Fourier-transform infrared spectroscopy (FT-IR) [Perkin-Elmer, model Paragon-500 spectrophotometer] Coin Cell (2016 type coin cell (Hohsen Co., Japan) assembled using lithium metal as anode, Celgard 2400 as separator, and 1 M solution of LiPF₆ in a 50:50 (V/V) mixture of ethylene carbonate/diethylene carbonate [ EC/DEC ] as electrolyte); Cell assembly (argon filled glove box [M Braun, Germany] with <2 ppm oxygen and moisture) and S W (Germany) Battery Testing System

2.11 Research Design and Methodology

The preliminary step is to synthesize the cathode materials from the metal salts and triple distilled water as solvent for both precursor and chelating agent. Prior to the calcination of the synthesised materials, the TG-DTA analysis of the gel precursors was first
performed. After the calcination, the physical characterisations of the synthesised materials were carried out. Then the electrochemical cell assembly in argon filled glove box and finally the electrochemical characterisations of the assembled cell are performed.