

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL**

**DEVELOPMENT OF QUATERNARY NICKEL RICH  
COBALT FREE CATHODE MATERIALS**



**M.Sc. THESIS**

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**Department of Materials Science and Engineering**

**Materials Science and Engineering Programme**

**JANUARY 2024**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

**NİKELCE ZENGİN DÖRTLÜ KOBALT İÇERMEYEN  
KATOT MALZEME GELİŞTİRİLMESİ**

**YÜKSEK LİSANS TEZİ**

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*To my family,*



## FOREWORD

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## ABBREVIATIONS

|               |                                    |
|---------------|------------------------------------|
| <b>BC</b>     | : Before Christ                    |
| <b>CNT</b>    | : Carbon Nanotubes                 |
| <b>CSP</b>    | : Combustion Spray Pyrolysis       |
| <b>DEC</b>    | : Diethyl Carbonate                |
| <b>DMC</b>    | : Dimethyl Carbonate               |
| <b>EC</b>     | : Ethylene Carbonate               |
| <b>ESP</b>    | : Electrostatic Spray Pyrolysis    |
| <b>EV</b>     | : Electric Vehicle                 |
| <b>FSP</b>    | : Flame Spray Pyrolysis            |
| <b>HEV</b>    | : Hybrid Electric Vehicle.         |
| <b>IEA</b>    | : International Energy Agency      |
| <b>LCO</b>    | : Lithium Cobalt Oxide             |
| <b>LIB</b>    | : Lithium-ion battery              |
| <b>Li-ion</b> | : Lithium-ion                      |
| <b>LNMO</b>   | : Lithium Nickel Manganese Oxide   |
| <b>LTO</b>    | : Lithium Titanate.                |
| <b>NCA</b>    | : Nickel Cobalt Aluminum Oxide     |
| <b>NMC</b>    | : Nickel Manganese Cobalt          |
| <b>NMP</b>    | : N-Methyl-2-pyrrolidon            |
| <b>PEO</b>    | : Polyethylene oxide               |
| <b>PHEV</b>   | : Plug-in Hybrid Electric Vehicle. |
| <b>PVDF</b>   | : Polyvinylidene Fluoride          |
| <b>RLC</b>    | : Residual lithium compound        |
| <b>SEI</b>    | : Solid Electrolyte Interface      |
| <b>SOC</b>    | : State of Charge                  |
| <b>TCO</b>    | : Titanium Cobalt Oxide            |
| <b>TM</b>     | : Transition Metal                 |
| <b>USP</b>    | : Ultrasonic Spray Pyrolysis       |
| <b>Zn-HgO</b> | : Zinc-Mercury Oxide               |



## SYMBOLS

|       |                             |
|-------|-----------------------------|
| \$    | : Dollar                    |
| €     | : Euro                      |
| °C    | : Degree Celsius            |
| Å     | : Angstrom                  |
| C     | : Current rate              |
| kWh   | : Kilowatt-hour             |
| mAh/g | : Milliampere-hour per gram |
| mL    | : Milliliter                |
| nm    | : Nanometer                 |
| Q     | : Charge                    |
| V     | : Volts                     |
| Wh/kg | : Watt-hour per kilogram    |
| μm    | : Micrometer                |



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## **DEVELOPMENT OF QUATERNARY NICKEL RICH COBALT FREE CATHODE MATERIALS**

### **SUMMARY**

Modern energy storage technology is led by lithium-ion (Li-ion) batteries, which power an array of electronic products and electric cars. Because of their great energy density, extended cycle life, and adaptability, they have completely changed the way we store and use energy. The three primary parts of Li-ion batteries are the electrolyte, cathode, and anode. Graphite is commonly used for the anode, and depending on the kind of battery, several materials can be used for the cathode. Typically, a lithium salt dissolved in a solvent serves as the electrolyte, facilitating the transfer of lithium ions between the anode and cathode during charge and discharge. Lithium ions travel through the electrolyte from the anode to the cathode during discharge, producing an electric current. On the other hand, when charging occurs, the movement of lithium ions from the cathode to the anode is inverted. Compared to other battery types, Li-ion batteries provide a number of benefits. First of all, they store more energy per unit weight or volume thanks to their high energy density. Li-ion batteries also hold their charge for longer periods of time due to their comparatively low self-discharge rate. Li-ion batteries also have a long cycle life and a high number of cycles of charging and discharging without seeing a noticeable reduction in capacity. They are a preferred option in the quickly developing field of energy storage due to their adaptability and suitability for uses ranging from electric vehicles to portable electronic devices.

Common cathode materials in commercial Li-ion batteries include lithium cobalt oxide ( $\text{LiCoO}_2$ ), lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ), lithium iron phosphate ( $\text{LiFePO}_4$ ) nickel cobalt manganese oxide (NCM) or nickel cobalt aluminium oxide (NCA).  $\text{LiCoO}_2$  is known for its high energy density,  $\text{LiCoO}_2$  batteries offer excellent performance but are expensive and can be prone to thermal runaway.  $\text{LiMn}_2\text{O}_4$  cathode material is more cost effective but has lower energy density and shorter cycle life compared to  $\text{LiCoO}_2$ .  $\text{LiFePO}_4$  has a longer cycle life but slower rate capability and theoretical capacity. NCM or NCA cathodes contain nickel, cobalt, manganese and aluminium. They strike an important balance between energy density, cost and safety. NCM cathodes are widely used in electric vehicles. High capacity values and very good speed capability are among their advantages. Their cycle life is lower than olivine or spinel structures such as  $\text{LiFePO}_4$ . Nickel in the structure acts as the centre of redox mechanisms during charging and discharging, while aluminium and/or manganese provide thermal and chemical stability. Cobalt, on the other hand, provides enhanced rate capability in the system and basically prevents capacity reduction by preventing the mixing of lithium and divalent nickel atoms, which tend to enter each other's regions in the crystal structure due to the similarity of their radii.

Today, the toxicity of cobalt, the fact that approximately 47% of its reserves are located in the Republic of Congo, the exploitation of child labour in its mines and the large fluctuations in economic pricing over the years have led to a desire to limit its use.

Therefore, the production of alternative cathode materials that do not contain cobalt is in question. Alternatives to cobalt-free cathode materials can be categorised under three main headings. These are nickel-rich, lithium-rich and spinel-olivine structures. Lithium-rich cathodes are highly prone to the formation of oxygen gas in the structure, phase transformations, oxidation of the electrolyte and reduction and dissolution of transition metals. Spinel structures have problems such as  $\text{Mn}^{3+}$  disproportionation, oxidation of the electrolyte and dissolution of transition metals. Nickel-rich cathode materials are prone to Ni/Li mixing, phase transformations, formation of residual lithium compounds (RLC), development of side reactants with RLC formation and dissolution of transition metals. Due to the aforementioned reasons, it is thought that a synergetic effect can be created by using manganese and aluminium together to provide thermal and chemical stability in addition to the development of a cobalt-free, nickel-rich cathode material due to the decreasing lithium reserves and increasing capacity requirement. Therefore, two different compositions of nickel-rich cathode materials with aluminium and manganese content in addition to iron were synthesised since their electronic configuration is similar to cobalt.

Two samples, NFAM-6211 and NFAM-8155, were also produced by co-precipitation method. The synthesis was carried out using sulfate-based precursor materials under nitrogen atmosphere, pH in the range of 11.30-11.5, feeding rates of 0.3-0.5 mL/min and mixing at 500 rpm for one day. The synthesised cathode materials in the form of hydroxides were filtered and washed in centrifuge and filter paper, then dried and heat treated. Calcination was carried out in both oxygen atmosphere and open atmosphere at 500°C, 6 hours and 750°C, 12 hours. Finally, the active material in oxide form was obtained. XRF, XRD and SEM/EDS analyses of the obtained active materials were performed. XRF analysis showed some deviation from the intended chemical composition and impurities such as Si and S were detected. At the same time, it was observed from these results that the washing method was better when the washing method was performed with filter paper. In the XRD analysis, it was determined that the samples obtained had a layered structure due to the splitting of (006)/(012) and (018)/(110) peaks. When the experiments performed in open atmosphere and oxygen atmosphere (1 bar, 30 mL/min) were compared, it was observed that the calcination process performed in open atmosphere caused lithium loss due to oxygen deficiency in the structure. This interpretation was made by looking at the intensities of (003) and (104) peaks, and it was found that this ratio was 0.7, which is far from the minimum value of 1.2. Therefore, it was concluded that calcination should be carried out under oxygen atmosphere. Both structures are of  $\alpha\text{-NaFeO}_2$  type (space group R-3m). Based on XRD data, Rietveld analysis was performed for both synthesised samples. In the analyses, although the mixing ratio in the structure is at the desired levels, it was determined that a significant part of the iron and nickel atoms are in the 3a regions. In NFAM-6211 material, about 8.2% of all nickel atoms in the structure replaced lithium atoms, while about 2% of iron atoms replaced lithium atoms. For NFAM-8155, these data are 7.8% and 0.4%, respectively. Although NFAM-8155 has a higher nickel content, the reason why Li/Ni mixing is less common is the high iron content of NFAM-6211. Increasing iron content reduces the amount of lithium atoms in the 3a region, which is thought to have a significant negative effect on electrochemical performance. At the same time, with increasing iron content, the lattice parameters of the structure increased and caused the structure to be larger in volume. The reason for some peak shift in XRD data is thought to be sulfur from the precursor materials. In the EDS spectrum, the peak of sulphur with a value of approximately 2.3 kV is visible. When SEM/EDS analyses are examined, NFAM-6211 shows agglomerations formed

by morphologically more plate-like structures, while NFAM-8155 shows more spherical agglomerations. Therefore, NFAM-8155 is more likely to have a denser structure. The atomic amounts of the elements in the structure are similar to the mole fractions calculated according to XRF results. However, when the distribution of the elements is examined, it is seen that NFAM-6211 has a more heterogeneous distribution than NFAM-8155 and has more dense or less dense regions in the elemental sense. Especially aluminium has a much less homogeneous distribution in both samples. According to SEM/EDS results, NFAM-8155 has better elemental content, better morphological surface and more homogeneous distribution.





## NİKELCE ZENGİN DÖRTLÜ KOBALT İÇERMİYEN KATOT MALZEME GELİŞTİRİLMESİ

### ÖZET

Lityum-iyon (Li-iyon) piller, modern enerji depolama teknolojisinin ön saflarında yer almakta ve çok çeşitli elektronik cihazlara ve elektrikli araçlara güç sağlamaktadır. Bu piller, yüksek enerji yoğunlukları, uzun çevrim ömürleri ve çok yönlülükleri sayesinde enerjiyi depolama ve kullanma şeklimizde devrim yaratmıştır. Li-ion piller üç ana bileşenden oluşur: bir anot, bir katot ve bir elektrolit. Anot tipik olarak grafitten yapılırken, katot pil türüne bağlı olarak çeşitli malzemelerden oluşur. Şarj ve deşarj sırasında lityum iyonlarının anot ve katot arasındaki hareketini kolaylaştıran elektrolit, genellikle bir çözücü içinde çözünmüş bir lityum tuzudur. Deşarj sırasında lityum iyonları elektrolit aracılığıyla anottan katoda doğru hareket ederek elektrik akımı oluşturur. Buna karşılık, şarj sırasında, lityum iyonları katottan anoda geri göç ederken süreç tersine döner. Li-ion piller diğer pil türlerine göre çeşitli avantajlar sunar. İlk olarak, birim ağırlık veya hacim başına daha fazla enerji depolama kapasitesi sağlayan yüksek bir enerji yoğunluğuna sahiptirler. Ayrıca, Li-ion piller nispeten düşük bir kendi kendine deşarj oranı sergiler, yani şarjlarını uzun süreler boyunca korurlar. Ayrıca, Li-ion piller uzun bir çevrim ömrüne sahiptir ve önemli bir kapasite kaybı yaşamadan çok sayıda şarj ve deşarj döngüsüne dayanır. Taşınabilir elektronik cihazlardan elektrikli araçlara kadar çeşitli uygulamalar için çok yönlülükleri ve uygunlukları, onları hızla gelişen enerji depolama alanında tercih edilen bir seçenek haline getirmektedir.

Ticari Li-ion pillerdeki yaygın katot malzemeleri arasında lityum kobalt oksit ( $\text{LiCoO}_2$ ), lityum mangan oksit ( $\text{LiMn}_2\text{O}_4$ ), lityum demir fosfat ( $\text{LiFePO}_4$ ) nikel kobalt mangan oksit (NCM) veya nikel kobalt alüminyum oksit (NCA) bulunur.  $\text{LiCoO}_2$  yüksek enerji yoğunluğu ile bilinir,  $\text{LiCoO}_2$  piller mükemmel performans sunar ancak pahalıdır ve termal kaçak eğilimli olabilir.  $\text{LiMn}_2\text{O}_4$  katot malzemesi daha uygun maliyetlidir ancak  $\text{LiCoO}_2$ 'ye kıyasla daha düşük enerji yoğunluğuna ve daha kısa çevrim ömrüne sahiptir.  $\text{LiFePO}_4$  daha uzun çevrim ömrüne sahip olmasına karşın daha yavaş hız kabiliyetine ve teorik kapasiteye sahiptir. NCM veya NCA katotları ise nikel, kobalt, mangan ve alüminyum içerir. Enerji yoğunluğu, maliyet ve güvenlik arasında önemli bir denge kurarlar. NCM katotları elektrikli araçlarda yaygın olarak kullanılmaktadır. Yüksek kapasite değerleri ve oldukça iyi hız kabiliyeti avantajlı oldukları konular arasında sayılabilir. Çevrim ömürleri ise  $\text{LiFePO}_4$  gibi olivin veya spinel yapılara göre düşüktür. Yapıda bulunan nikel, şarj ve deşarj sırasında redoks mekanizmalarının merkezi olarak görev alırken, alüminyum ve/ya mangan termal ve kimyasal kararlılığı sağlar. Kobalt ise sistemde gelişmiş hız kabiliyeti özelliği sağlayıp, temel olarak yarıçaplarının benzerliğinden dolayı kristal yapıda birbirlerinin bölgelerine girme eğiliminde olan lityum ve iki değerlikli nikel atomlarının karışmasını önleyerek kapasite düşüşünün önüne geçer.

Günümüzde kobaltın toksik olması, rezervlerinin yaklaşık %67'sinin Kongo Cumhuriyetinde yer alması, madenlerinde çocuk işçilerin istismar edilmesi ve ekonomik açıdan fiyatlandırma hususunda yıllardır süre gelen büyük dalgalanmalar ile beraberinde maliyeti arttırması dolayısıyla kullanımını sınırlandırma isteğine yol açmaktadır. Bu yüzden, kobalt içermeyen alternatif katot malzemelerin üretimi söz konusudur. Kobalt içermeyen katot malzemelerin alternatifleri üç ana başlık altında toplanabilir. Bunlar, nikel bakımından zengin, lityum bakımından zengin ve spinel-olivin yapılarıdır. Lityum bakımından zengin katotlar yapıda oksijen gazının oluşumuna, faz dönüşümlerinin gerçekleşmesine, elektrolitin oksidasyonuna ve geçiş metallerinin indirgenmesi ve çözünmesine oldukça meyillidir. Spinel yapılar ise  $Mn^{3+}$  disproporsiyonlaşması, elektrolitin oksidasyonu ve geçiş metallerinin çözülmesi gibi sorunlara sahiptir. Nikel bakımından zengin katot malzemelerine bakıldığında ise Ni/Li karışımı, faz dönüşümleri, kalıntı lityum bileşenlerinin (RLC) oluşumu, RLC oluşumu ile beraber yan reaksonların gelişmesi ve geçiş metallerinin çözülmesi gibi sorunlar ile karşı karşıya kalınmaktadır. Yukarıda bahsi geçen sebeplerden dolayı kobalt içermeyen, azalan lityum rezervleri ve artan kapasite ihtiyacı gerekliliğinden dolayı nikel bakımından zengin katot malzemesi geliştirilmesine ek olarak termal ve kimyasal kararlılığı sağlamak adına kullanılan mangan ve alüminyumun bir arada kullanılması ile sinerjistik bir etki yaratılabileceği düşünülmüştür. Dolayısıyla nikel bakımından zengin, elektronik konfigürasyonu kobalt ile benzer olduğundan demire ek olarak alüminyum ve mangan içeriğine sahip iki farklı kompozisyonda katot malzemesi sentezlenmiştir.

NFAM-6211 ve NFAM-8155 kodlu iki numune de birlikte çöktürme metodu ile üretilmiştir. Sentez, azot atmosferi altında, pH'ı 11.30-11.5 aralığında, 0.3-0.5 mL/dakika besleme hızlarında ve bir gün boyunca 500 rpm'de karışacak şekilde sülfat bazlı öncül malzemeler kullanılarak gerçekleştirilmiştir. Sentezlenen hidroksit formundaki katot malzemeleri, santrifüjde ve filtre kağıdında filtrelenip yıkandıktan sonra kurutulup ısıtılma işlemine tabi tutulmuştur. Kalsinasyon hem oksijen atmosferi ve açık atmosferde 500°C, 6 saat ve 750°C, 12 saat olacak şekilde gerçekleştirilmiştir. Nihai olarak oksit haldeki aktif malzeme elde edilmiştir. Elde edilen aktif malzemelerin XRF, XRD ve SEM/EDS analizleri yapılmıştır. XRF analizinde üretilmesi amaçlanan kimyasal kompozisyondan bir miktar sapma görülmüş ve Si, S gibi safsızlıklar tespit edilmiştir. Aynı zamanda bu sonuçlardan yıkama metodunun filtre kağıdı ile yapıldığı durumda daha iyi olduğu gözlemlenmiştir. Yapılan XRD analizinde ise elde edilen numunelerin (006)/(012) ve (018)/(110) piklerinde meydana gelen bölünmeden dolayı katmanlı yapıda olduğu tespit edilmiştir. Açık atmosfer ve oksijen atmosferinde (1 bar, 30 mL/dakika) yapılan deneyler kıyaslandığında, açık atmosferde yapılan kalsinasyon işleminin yapıda oksijen yetersizliğinden dolayı meydana gelen lityum kaybına yol açtığı görülmüştür. Bu yorum (003) ve (104) piklerinin şiddetlerine bakılarak yapılmış, bu oranın olması gereken minimum 1.2 değerinden oldukça uzak 0.7 değerinde olduğu tespit edilmiştir. Dolayısıyla, kalsinasyonun oksijen atmosferi altında yapılmasının gerekli olduğu sonucuna varılmıştır. Her iki yapı da  $\alpha$ -NaFeO<sub>2</sub> tipinde (uzay grubu R-3m) yapıdadır. XRD verilerinden hareketle sentezlenen her iki numune için de Rietveld analizi yapılmış. Analizlerde, yapıdaki karışım oranı her ne kadar istenilen seviyelerde olsa da, demir ve nikel atomlarının önemli bir kısmının, 3a bölgelerinde olduğu tespit edilmiştir. NFAM-6211 malzemesinde yapıdaki tüm nikel atomlarının yaklaşık 8.2%'si lityum atomlarının yerini alırken, demir atomlarının yaklaşık %2'si lityum atomlarının yerini almıştır. NFAM-8155 için ise bu veriler sırasıyla %7,8 ve %0,4'tür. NFAM-8155'in daha yüksek nikel miktarına sahip olmasına karşın, Li/Ni karışımının daha az

görölmesinin sebebi NFAM-6211'in yüksek demir içeriğidir. Artan demir içeriği, 3a bölgesindeki lityum atomlarının miktarını azaltmaktadır ve dolayısıyla bu durumun elektrokimyasal performansa önemli derecede negatif yönde etki ettiğı düşünölmektedir. Aynı zamanda artan demir içeriğı ile beraber yapının kafes parametrelerinde artış meydana gelmiş ve yapının daha büyük hacimli olmasına sebep olmuştur. XRD verilerinde meydana gelen bir miktar pik kaymasının sebebi ise öncöl malzemelerden gelen kükört olduğı düşünölmektedir. EDS spektrumunda kükördün yaklaşık 2.3 kV değeriindeki piki gözökmektedir. SEM/EDS analizlerine bakıldığında ise NFAM-6211 morfolojik olarak daha plaka benzeri yapıların oluşturduğı aglomerasyonlar görölürken, NFAM-8155 için daha küresel aglomerasyonlar görölmüştür. Doalyısıyla NFAM-8155 daha yoğun bir yapıya sahip olması daha olasıdır. Yapıdaki elementlerin atom miktarlarına bakıldığında XRF sonuçlarına göre hesaplanan mol fraksiyonları ile benzerlik görölmektedir. Ancak elementlerin dağılımına bakıldığında, NFAM-6211'in NFAM-8155'e göre daha heterojen şekilde dağılıma ve elementel anlamda yer yer daha yoğun veya daha az yoğun bölgelere sahip olduğı görölmektedir. Özellikle alüminyumun çok daha az homojen dağılıma sahip olduğı her iki numunede de görölmüştür. SEM/EDS sonuçlarına göre, NFAM-8155 daha iyi element miktarına, daha iyi morfolojik yüzeye ve daha homojen bir dağılıma sahiptir.



## **1. INTRODUCTION**

ion (Li-ion) batteries are rechargeable batteries that are commonly utilized in handheld gadgets, electric cars, and renewable energy storage facilities [1]. Because of their extended lifespan, minimal self-discharge rate, and high energy density, they are favored over other battery types. They are becoming the go-to power source for portable electronics because of their enormous potential to provide efficient energy storage and sustainable environmental practices [2], such as smartphones and laptops. Li-ion batteries are preferred over Ni-Cd batteries for a long period of time as the industry leader [3]. They are being used both in hybrid and fully electric vehicles. Also, increasingly being used in renewable energy systems such as solar and wind power as a storage where excess energy generated by these systems during peak production times are stored and used during periods of low production. In addition to these areas, lithium-ion batteries are also used in aerospace, satellites, unmanned aerial vehicles, and other applications where weight and size are critical factors.

Li-ion battery fundamental research dates back to the 1970s, and during the 1980s, significant progress has been made [4]. The most common combination is found in gadgets that are portable, where it is used as the anode of graphite and the cathode of lithium cobalt oxide. Other cathode materials include lithium nickel manganese cobalt oxide, lithium iron phosphate and lithium manganese oxide. Although Li-ion batteries are expensive and have a lesser energy density than gasoline, ongoing research goes on for reducing the cost of the battery and as well as increasing the energy density, improving cycle life and charging time [3]. Overall, the importance and usage areas of lithium-ion batteries are vast, and they are a critical component of modern-day technology.

### **1.1 Historical Background**

An electrochemical cell is a device that converts energy released in a chemical reaction into electrical current. An apparatus that transforms chemical reaction energy into electrical energy is called an electrochemical cell. The earliest battery is said to have

been created as Baghdad Batter in the first century BC [4], but the electrochemical cell wasn't widely known until the invention of Luigi Galvani and Alessandro Volta at the end of the eighteenth century. The disagreement between the two scientists was brought to light by Galvani's experiment involving a frog's leg twitching when touched by two different metals. He thought animals could generate electricity, while Volta argued that his voltaic pile formed by alternating metal disks with a sodium chloride solution in between could create energy. The two theories are not necessarily contradictory, as Galvani's could be related to bio-energy and Volta's to energy storage [5].

The battery invented by Georges-Lionel Leclanché was first shown in 1866. It consisted of an aqueous solution of ammonium chloride with a zinc rod working as the negative electrode and a mixture of carbon and manganese oxide working as the positive electrode. These batteries, often referred to as alkaline and carbon-zinc cells, are still in usage nowadays. The lead-acid rechargeable battery was created by Gaston Planté in 1859, while the nickel-cadmium rechargeable battery was created by Waldmar Jungner in 1901. These two systems are the basis of modern commercial batteries [5].

For over a century, there was little progress in the field of batteries, as the early designs by Leclanché, Jungner, and Planté were sufficient for the technology of the time. But in the late 1960s, when implanted medical devices became more common, military operations needed high-energy and high-power sources, and the consumer electronics industry grew rapidly, there was an unexpected need for portable energy. These developments highlighted the main limitations of existing batteries, which had low energy density and specific capacity, leading to low energy-to-weight and energy-to-volume ratios. One example of this was the use of primary Zn-HgO batteries in early pacemakers, which were heavy and bulky and required replacement every two years through surgery [5]. The solution to these problems came with the development of lithium-iodine batteries, which had a much higher theoretical specific capacity than zinc batteries and could provide a practical energy density of around 250 Wh/kg, nearly five times higher than Zn-HgO batteries [6].

There were two ways to enhance the performance of batteries based on lithium: either swapping out the lithium metal for a less reactive anode material, or carefully choosing the electrolyte system to maximize lithium deposition. The first alternative was shown

in 1978 by Armand, who suggested using a polymer electrolyte that was without solvent and composed of a compound between a coordinating polymer and a lithium salt [7]. This was utilized to construct a big laminated battery unit by Hydro Québec and 3M using a vanadium oxide cathode, a PEO-based electrolyte, and a lithium foil anode. However, a more stable anode was needed. The solution was to use a "rocking chair" design, with two intercalation electrodes that could accept and release lithium ions during charge and discharge, respectively. This concept had been proposed in the late 1970s and demonstrated in the early 1980s, but it took until 1991 for it to be used in a practical application, the lithium ion battery developed by Sony [8–11]. Using lithium cobalt oxide, which Goodenough first revealed with  $\text{LiCoO}_2$  in 1980, as the "lithium supply" cathode and graphite as the "lithium sink" anode, this battery was created [5]. The work of Sony sparked widespread interest, leading to the production of renamed lithium ion batteries by many manufacturers, mainly in Asia.

Battery industry is currently focused on developing new concepts that increase safety, reduce cost, and significantly increase energy density, with a particular emphasis on improving energy density. This is a difficult task, but it is considered a top priority by many developed countries around the world, who are investing heavily to achieve these goals. Two potential candidates for high-energy-density batteries are the lithium-sulfur and lithium-air batteries, which have theoretical energy densities of 2,600 Wh/kg and 11,400 Wh/kg, respectively [5]. However, there are still many challenges to overcome before these batteries can become viable.

## **1.2 Economical Aspects of Lithium-Ion Battery**

A BloombergNEF (BNEF) investigation found that the average price of a Li-ion EV battery pack decreased by 89% from \$1200/kWh in 2010 to \$132/kWh in 2020. By 2021, it is expected that the pack price will be less than \$100/kWh [12]. By 2027, it is anticipated that the world demand for electric car batteries will have grown to \$225.55 billion, due to the need for more environmentally friendly transportation and growing climate change concerns [13]. Solid-state batteries are anticipated to be expensive during the early stages of development, but if their energy density is twice, they may dramatically lower the cost of EVs. For instance, a Tesla Model S's range might be increased to 1000 km or its cost may be cut in half [14]. The increase in sales volumes is expected to lead to a decrease in the range of €188 to €200 per kilowatt-hour (kWh)

by 2030. [15], resulting in competitive CO2 abatement costs. Additionally, some initiatives in North American battery industry are given in Figure 1.1 to observe growing sector.



**Figure 1.1 :** Initiatives in North American battery industry [12].

An important part of lithium-ion batteries, the world's lithium resources are thought to be 14 million tons. From 2008 and 2018, the top producing nations' yearly output increased from 25,400 to 85,000 tons. China produced 14,000 tons of lithium in 2021, Chile produced 26,000 tons, and Australia produced 55,000 tons [16]. Bolivia (21 million tons), Argentina (19 million tons), and Chile (9.8 million tons) are the countries with the highest lithium reserves, respectively [16–18]. Distribution of production and reserves of lithium is given Figure 1.2.



**Figure 1.2:** General lithium reserves and production data all over the world [19].

High-surface lithium deposits pose a significant safety risk for Li-ion batteries, and their extraction has negative long-term effects. It's crucial to guarantee a long - term

supply of all raw materials since desire for lithium is rising as a result of its usage in evs as well as other clean energy technologies like wind turbines and solar panels [19]. There are different reserve situations worldwide for common metals like lithium, cobalt, and nickel that are utilized e.g. in NMC cathode materials [20]. The demand for these components is anticipated to increase dramatically in the upcoming years due to the growing use of renewable energy technologies, as reported by the International Energy Agency (IEA). As cathode chemistries migrate away from NMC 111 towards lower-cobalt chemistries (NMC 622 and NMC 811), it is projected that need for nickel would grow by 41 times and that of cobalt by 21 times [21]. Material costs in a general lithium ion battery are evaluated in aspect of their all production process and components respectively Figure 1.3 and Figure 1.4.

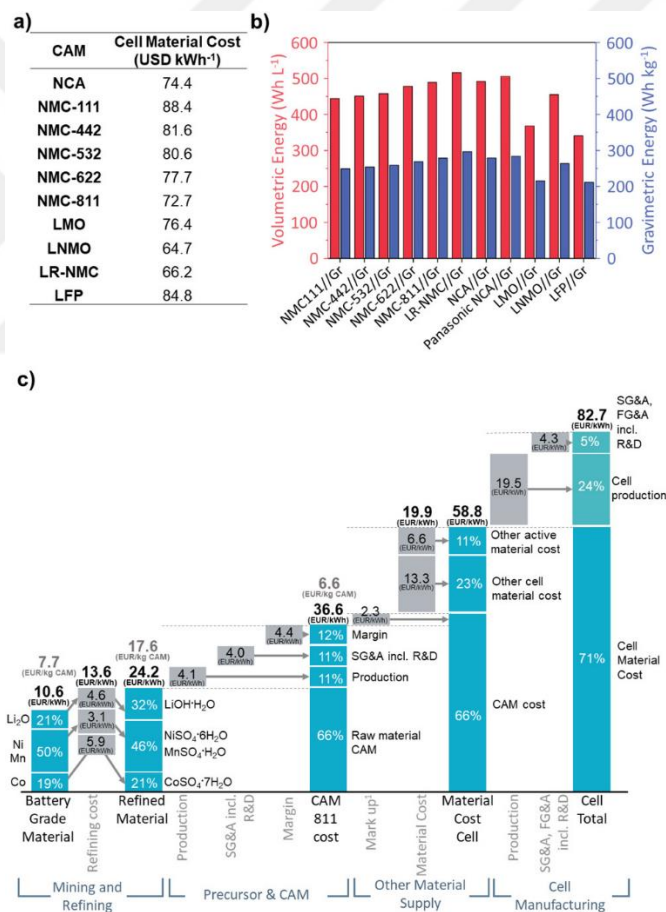


**Figure 1.3:** (a) Material costs for most common used cathodes. (b) Volumetric and gravimetric energy values for regarding cathode materials with graphite anode. (c) All cost distribution over all process for a NMC cathode material to produce a prismatic cell in China [20].

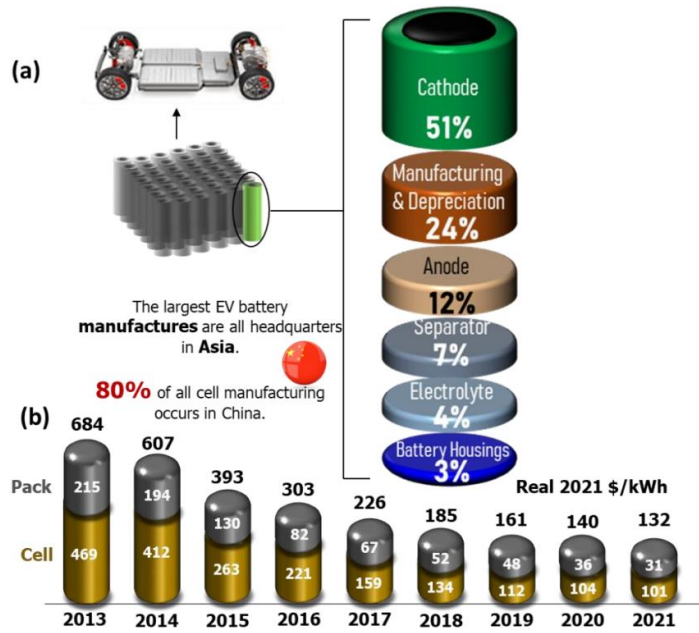


**Figure 1.4:** (a) Diagram detailing an EV battery material's cost. (b) Volume-weighted average price split for packs and cells [12].

### 1.3 Working Mechanism of Lithium Ion Battery

A battery cell is responsible for converting chemical energy into electrical energy. The basic components involved in this energy conversion are the cathode, anode and electrolyte. The anode and cathode materials in the cell are the electrodes where redox reactions take place, while the electrolyte is the medium that surrounds these electrodes and provides ionic movement. As an example, electrochemical system with  $\text{LiCoO}_2$  cathode and graphide anode is shown in Figure 1.5.

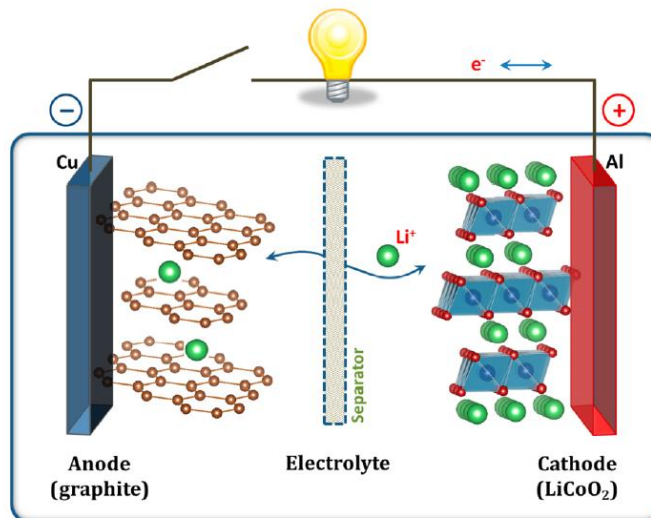


**Figure 1.5:** An electrochemical cell system [22].

A cathode is a structure that can contain, for example, the working cation (e.g. lithium) reversibly in its structure and in the process create an infinite solid-solution gap. The solid-solution gap may decrease as the velocity of the working ion increases, resulting in higher currents. This reduces the expected time-dependent charge transfer. In addition, the energy difference between the LUMO and HOMO of the electrolyte determines the maximum voltage that can be operated. The maximum stable voltage value is 1.5 V for a liquid electrolyte medium. The higher this value, the higher the energy density that can be stored. The external potential difference between anode and cathode can increase the voltage. However, the inevitable passive surface layer must not impede the movement of the lithium ion and must be able to adapt to the change in surface size caused by the volume change during cycling. This passive film creates an impedance to the movement of lithium at the electrode and electrolyte interface, which leads to a decrease in the performance of the battery cell. In addition, the formed passive film can incorporate the lithium in the structure, which can cause an irreversible performance degradation.

In order to contribute to this process, scientists have focused on controlling the electrode passive film, improving the movement of lithium across the interface, finding an electrolyte that can operate in the high voltage range and whose ionic conductivity does not decrease, reducing the size of the active particles, reducing the cost, finding high-capacity and safe anode material, fast charging and alternative cathode material research. The reasons for all these studies can be summarized in two main reasons reducing fossil fuel imports and reducing CO<sub>2</sub> emissions that cause global warming.

Solid electrolytes are utilized with gas or liquid electrodes. They can also be utilized with solid electrodes; however, unless the solid electrolyte is polymeric or the solid electrode is thin, the solid-solid contact may provide significant challenges. The electrodes are kept apart by the employment of an electrolyte-liquid separator. The external electric current is produced by the ionic flow between the cathode and the anode. This is because the ionic mobility is very small compared to the electrical conductivity.

During charging and discharging, the internal impedance in the battery increases against the ionic current and decreases the discharge voltage from the open circuit

voltage while increasing the charge voltage to make the chemical reaction reversible. This polarization during charging and discharging can be expressed respectively as equation (1.1) and equation (1.2). Thus, the voltages can be expressed as in equation (1.3) and equation (1.4). The "q" expression in the formulas indicates the state of charge.

$$\eta = I_{\text{dis}} R_b \quad (1.1)$$

$$\eta = I_{\text{ch}} R_b \quad (1.2)$$

$$V_{\text{dis}} = V_{\text{oc}} - \eta(q, I_{\text{dis}}) \quad (1.3)$$

$$V_{\text{ch}} = V_{\text{oc}} + \eta(q, I_{\text{ch}}) \quad (1.4)$$

The energy storage efficiency of the cell at a given current value can be expressed as in equation (1.5) and equation (1.6).

$$100 \times \frac{\int_0^{Q_{\text{dis}}} V_{\text{dis}}(q) dq}{\int_0^{Q_{\text{ch}}} V_{\text{ch}}(q) dq} \quad (1.5)$$

$$Q = \int_0^{\Delta t} I dt = \int_0^Q dq \quad (1.6)$$

It can be expressed as The Q value is highly dependent on the I value. Because the interface between the electrode and the electrolyte is diffusion controlled at high currents. At high charge and discharge rates, diffusion-induced lithium ion loss exhibits a decrease in recoverable capacity. However, during cycling, electrode volume change, chemical reactions between the electrode and the electrolyte, and electrode degradation can cause unrecoverable capacity drops. The non-reversible SEI film formed in the discharge state between the electrode and the electrolyte can be distinguished from these unrecoverable capacity drops. Coulombic efficiency can be calculated from equation (1.7).

$$\text{Coulombic Efficiency} = 100 \times \frac{Q_{\text{dis}}}{Q_{\text{ch}}} \quad (1.7)$$

The cycle life is expressed as the number of times the battery reaches 80% of its initial reversible capacity. The energy value obtained with this capacity can be expressed as equation (1.8).

$$\text{Energy} = \int_0^{\Delta t} IV(t)dt = \int_0^Q V(q)dq \quad (1.8)$$

The cathode materials, which perform the oxidation task during charging, will be examined in more detail in the following sections since the main subject of this study is based on the cathode material. The other component of the battery, the anode material, should have improved electrochemical performance characteristics such as cycling, charging speed and energy density. This also applies to cathode materials. Historically, carbon-based materials were first commercialized in anode materials and these carbon-based materials are the most widely used anode materials in the industry today. Especially since graphitic carbon has a layered structure, it facilitates the movement of lithium in the system and offers very good cycling properties. However, the theoretical capacity value of carbon anodes is 372 mAh/g with the developing technology. In addition to the increasing need for energy and power density, the issue of safety is also an issue that draws attention to the use of carbon anode materials, especially in electric vehicles [22]. In 1997, Fuji Film introduced TCO material as an alternative to carbon-based anodes, but it was not successful due to its poor cycling characteristics [23]. Later, Sony accelerated the studies on anode materials with Sn-Co-C based amorphous or microcrystalline material, which was introduced to the market in 2005.

In addition to tin, silicon seems to be a good alternative for anode materials to store lithium. Since these elements work through an alloying mechanism, they cause large volumetric changes in the material, resulting in large stresses or strains in the structure. As a result, the so-called pulverization occurs, which results in degradation of the structure and disintegration of the material. As a result of pulverization, the battery may even become unusable after a few cycles. This problem has led to the use of composite materials as an alternative to battery anode materials. The reason for the choice of composite materials is that elements such as carbon, for example, absorb stresses, while elements such as tin or silicon allow for capacity increase. This will allow for higher capacity than carbon and better cycle life than silicon [3].

Carbons that can reversibly incorporate lithium can be broadly divided into graphitic and nongraphitic carbons. While graphitic carbons such as natural or synthetic graphites have a layered structure, disordered carbons, which do not have long distances and have a planar hexagonal structure, normally have high capacity values,

but experience a large capacity drop after the first cycle [24]. The reason for this situation is the growth of SEI formation, which is a passive film on the carbon surface after the first cycle and occurs due to the degradation of the electrolyte at low potential values, and then increases the impedance in the battery [24].

Other carbon-based materials are buckminsterfullerene, graphene and carbon nanotubes. Especially carbon nanotubes show very good conductivity due to their linear structure and facilitate the placement of lithium atoms [25], [26]. However, today's studies are not using pure CNT or graphene alone, but together because of their higher capacity. These carbon derivatives are shown in Figure 1.6.

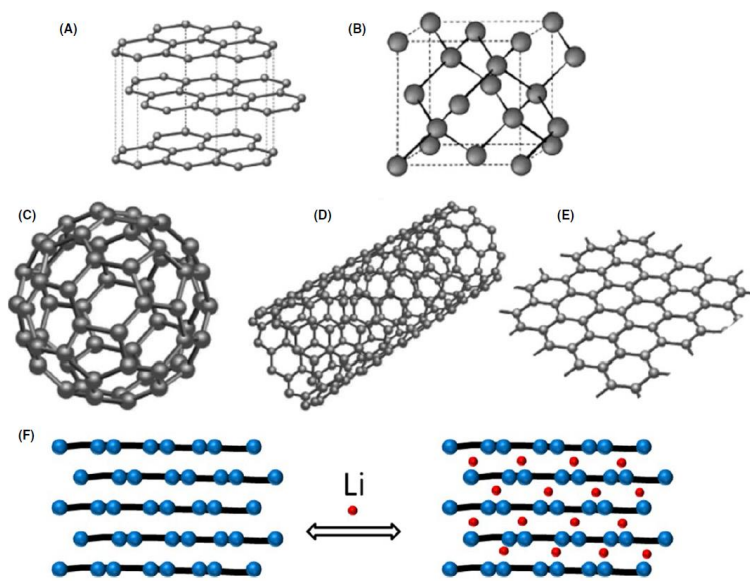


**Figure 1.6:** (a) Graphite consisting graphene layers. (b) Carbon atoms in diamond structure. (c) Buckminsterfullerene C60 in sphere structure. (d) CNT structure. (e) Graphene layer. (f) Insertion and extraction lithium [27].

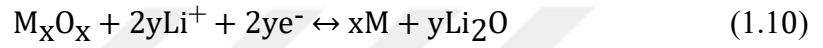
Another high capacity anode material is metal oxides. Although metal oxides have low electrical conductivity, this can be improved by nanoscale processing. The entry and exit of lithium in metal oxides can be evaluated under three different mechanisms. These mechanisms are insertion/extraction, alloying/dealloying and conversion. An example of the insertion/extraction mechanism is anatase  $\text{TiO}_2$  [28]. Most spinel or layered cathode materials also fit this mechanism. Alloying mechanism is formed by alloying elements such as Si, Sb, Ge, B, Sn with lithium and as a result, very high capacity values are achieved. However, as a result of this mechanism, up to 300% volumetric change is observed in the structure and this causes pulverization and a decrease in capacity. The last mechanism, the conversion mechanism, is usually seen

in anode materials containing transition metals. While these anode materials also show relatively high capacity values, each metal can combine with more than one lithium.  $\text{Li}_2\text{O}$  can be formed in this process and these metal oxide structures can also cause pulverization, reducing electrochemical performance [3]. These three mechanisms can be expressed respectively by the following equations and schematic representations in equations (1.9), (1.10), (1.11) and Figure 1.7.

Insertion reaction mechanism:



Li-alloy reaction mechanism:



Conversion reaction mechanism:

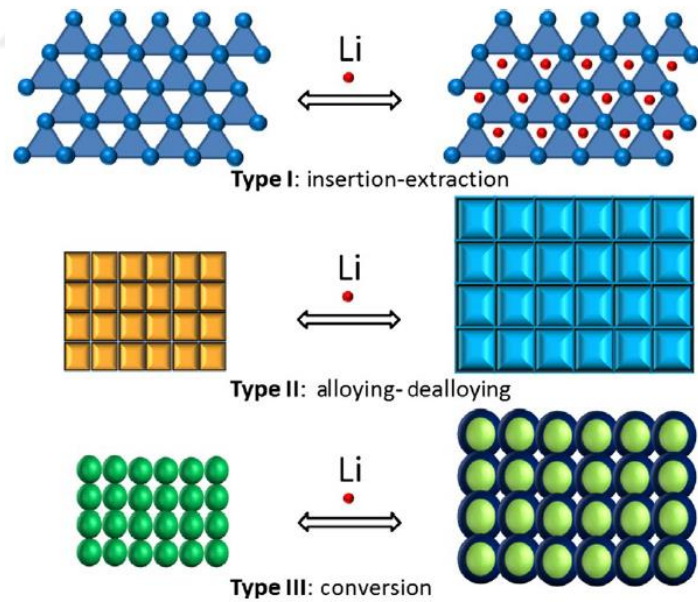
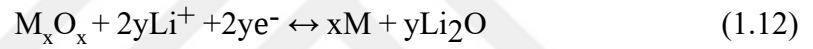


**Figure 1.7:** Mechanisms of lithium incorporation in the charging and discharging process of anode materials [29].

The electrolyte must be carefully selected as it must be resistant to any degradation despite the redox reactions occurring in the operating voltage range. In addition, the selected electrolyte must be inert and stable at operating temperatures. The electrolytes in lithium ion batteries are usually lithium salts dissolved in an organic solvent.

However, since these organic solutions are volatile and toxic flammable materials, they can cause thermal runaway and short circuits in the cell under certain conditions. Polar aprotic organic solvents such as carbonate solvents with high dielectric coefficients are preferred for the solvent to form compounds with lithium salts at high concentrations. In addition, solvents should have low viscosity and melting temperature to ensure sufficient ionic mobility in the temperature range studied. Solvents including propylene carbonate, ethylene carbonate, diethoxyethane, dioxolane,  $\gamma$ -butyrolactone, tetrahydrofuran, dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are accessible for this purpose. As for lithium salts, different lithium salts such as  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$  and  $\text{LiCF}_3\text{SO}_3$  can be preferred. Anions should be chosen so that they do not oxidize on the surface of the cathode.  $\text{LiPF}_6$  is the most commonly used salt among them. This is because of its conductivity, safety, and equilibrium between dissociation coefficient and ionic mobility. On the other hand,  $\text{LiPF}_6$  reacts readily with water to produce the very caustic chemical HF. As a result, a cell's moisture content when utilizing  $\text{LiPF}_6$  is crucial.

Solvents are mixed and formulated according to their viscosity, conductivity, chemical stability and ability to work with the selected lithium salt. For example, high dielectric coefficient and high viscosity solvents are usually mixed with low viscosity solutions. This is because the electrolyte must remain liquid in the temperature range studied. Usually 1M  $\text{LiPF}_6$  is dissolved in 50:50 w/w EC and DEC/DMC. Here EC has a high melting and boiling temperature while DEC or DMC has a low melting and boiling temperature. In general, EC binds more strongly to  $\text{Li}^+$  ions. In addition to all these, there may be different additives in the electrolyte to increase the stability of the electrolyte and to ensure a good SEI formation. Because the SEI formed in the first cycle prevents further degradation between the electrode and the electrolyte in future cycles.

Polymer, gel and ceramic electrolytes can also be used as an alternative to liquid electrolytes. Polymer electrolytes are high molecular weight-based polymers containing dissolved lithium salt and are solvent-free [30]. The advantages of polymer electrolytes over water electrolytes are that they have low volatility and are therefore safer, offer design flexibility and can eliminate the separator. It can also reduce cost.

They typically have conductivity values of  $10^{-8}$  S/cm, much lower than liquid electrolyte.

Another type of electrolyte is the gel electrolyte in which both lithium salt and polar solvents are dissolved and added to networks of inactive high-molecular-weight-polymer. Leakage is not a problem in this type of gel electrolyte as the liquid phase is completely absorbed. The conductivity of this type of electrolyte is higher than polymer type electrolytes.

Recently ceramic electrolytes have attracted a lot of attention. The advantage of ceramic electrolytes is that they are safe because they do not contain any flammable organic solvents. This type of electrolyte can be used in batteries operating under high temperature conditions. Examples are portable orthopedic devices and batteries for medical instruments that need to be sterilized in an autoclave at high temperature and pressure. Another advantage of using ceramic electrolyte at high temperatures is that it can withstand the increased ionic conductivity at high temperatures and thus have higher ionic conductivity.

The separator is usually located in energy storage systems containing liquid electrolyte. The function of the separator is to prevent physical contact between the cathode and the anode, thus preventing a short circuit. At the same time, the separator must not block the passage of lithium ions and must be chemically stable and inert. In addition, it should be mechanically resistant to punctures and stresses and the pore opening should be smaller than 1 micrometer. Today, microporous polymer membranes are very common as separators. Other parameters to be considered when selecting microporous polymer membranes are thickness, shrinkage, permeability, wettability and cost. These membranes can also be designed as multilayer composites, which can shut down the battery during thermal runaway or short circuit. For example, if two different separators are considered, if one of them has a low melting temperature and the other has a high mechanical strength, the pores of the low melting point separator will close at high temperature, thus preventing the battery from working harder and catching fire. An example of this is the PP-PE-PP composite. The melting point of PE is  $135^{\circ}\text{C}$ , while that of PP is  $165^{\circ}\text{C}$ . In high temperature applications, inorganic membrane separators attract a lot of attention. Separators account for one fifth of the cost of a battery [3]. Some terms are given to understand terminology of lithium ion battery in Table 1.1.

**Table 1.1 : Basic terminological terms for lithium ion batteries.**

| Terms                    | Definitions                                                                                                                                                                        |
|--------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Voltage                  | The difference in electrical potential between the cathode and anode, often expressed in volts (V).                                                                                |
| Current                  | The electrical charge flow, expressed in amperes (A).                                                                                                                              |
| Capacity                 | The energy that a battery is capable of storing; this is commonly expressed in ampere-hours (Ah).                                                                                  |
| Specific Capacity        | The milliampere-hours per gram (mAh/g) unit of measurement used to express the amount of charge that a battery can hold per unit mass.                                             |
| Energy Density           | Capacity to store energy per mass or volume unit.                                                                                                                                  |
| Specific Energy          | Watt-hours per kilogram (Wh/kg) is the standard unit of measurement for the amount of energy that a battery can store per unit mass.                                               |
| State of Charge (SoC)    | The percentage of a battery's total capacity that is currently available for use.                                                                                                  |
| Depth of Discharge (DoD) | The proportion of the overall capacity of a battery that has been used up.                                                                                                         |
| State of Health (SoC)    | The measure of a battery's remaining capacity relative to its original capacity when new.                                                                                          |
| Coulombic Efficiency     | The ratio of the actual charge transferred during a battery cycle to the theoretical charge that should have been transferred, expressed as a percentage.                          |
| Cycle Life               | The quantity of cycles of charge and discharge that a battery may endure before experiencing a notable reduction in its capacity.                                                  |
| Capacity Retention       | The ability of a battery to retain its original capacity over time.                                                                                                                |
| C rate                   | Rate of discharge or charge relative to the battery's nominal capacity.                                                                                                            |
| Rate Capability          | The ability of a battery to discharge or charge at a certain rate, often measured in C-rates.                                                                                      |
| Capacity Fade            | The gradual loss of a battery's capacity over time and/or use.                                                                                                                     |
| Short Circuit            | A condition where a battery's positive and negative terminals come into direct contact, causing a sudden discharge of electrical energy and potentially leading to safety hazards. |
| Thermal Runaway          | A condition where a battery experiences uncontrolled temperature rise due to internal reactions or external factors, which can lead to safety hazards.                             |

## 2. LITERATURE REVIEW

LiCoO<sub>2</sub>, the first cathode commercialized in 1991, has a theoretical specific capacity of 273 mAhg<sup>-1</sup> and a practical specific capacity of 140 mAhg<sup>-1</sup> [4]. By this time, LiCoO<sub>2</sub> has been combined with many metals and introduced to the market as cathode materials such as NCM, NCA. The cathode accounts for about 50% of the cost of the battery cell and about 10% to 30% of this cost belongs to the element cobalt [8]. The fact that about two-thirds of the cobalt reserves are in Congo and that children work in cobalt mines makes the use of cobalt metal undesirable [9]. In recent years, the price of cobalt has ranged between 30000\$/t and 90000\$/t and the global production capacity of lithium ion batteries is projected to increase from 290 GWh in 2018 to 1700 GWh in 2028 [10]. Cobalt prices fluctuate between \$30,000 and \$90,000 in futures trading, indicating market instability. Producers of batteries find it challenging to plan for abrupt increases, and end users typically bear these increases. Figure 2.1 shows the worldwide supply/demand balance, reserve status, and changes in cobalt prices in futures.

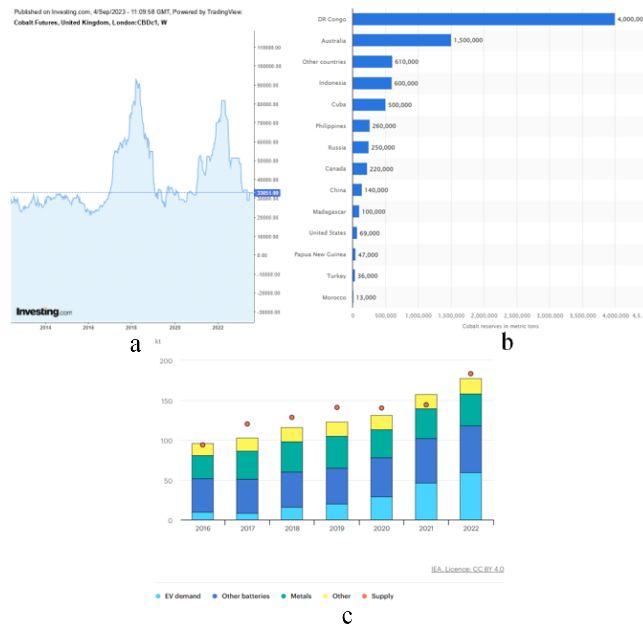


**Figure 2.1:** a) Price fluctuations of cobalt metal over the years b) Reserve distribution of cobalt metal in the world c) Sectoral distribution and supply of cobalt metal over the years [10].

When breathed or swallowed at above-average quantities (about 5 to 40 micrograms per day), cobalt is hazardous to humans. Chronic health issues including asthma, reduced lung function, heart enlargement, and liver and kidney congestion can result from cobalt poisoning. Even the reproductive system in both men and women is susceptible to it. The public is more at danger of issues as more lithium ion batteries find their way into wastewater systems, but those who mine and treat cobalt are the ones most at risk.

Zambia and the Democratic Republic of the Congo, two Central African nations lacking adequate environmental and public health regulations, supply a large portion of the world's cobalt. Up to 40,000 children as young as six years old may be working as miners in the Congo, where child labor is reported to be common. Mines are frequently dangerous, ill-ventilated, and prone to collapsing. Human rights organizations have also started to pay attention to the cobalt trade in Africa, and in nations like Australia and Cuba, cobalt mining continues to harm the environment. Therefore, it is important to first investigate the function of cobalt in cathode materials before looking for alternative cobalt-free cathode materials in order to avoid these circumstances. The current state of the world is causing a change in the trend toward cobalt-free cathode materials. For instance, Tesla said that cobalt will not be used in any upcoming electric car innovations.

At first glance,  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  stand out as alternatives to cobalt-free energy storage systems. However, although they have good thermal conductivity and low cost, they cannot be shown as a good candidate [15-16]. This is because  $\text{LiFePO}_4$  has poor electrical conductivity at low temperatures and voltage plateaus as low as 3.3 V. This also limits the energy density. Besides  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$  also experiences a large volumetric change during cycling due to  $\text{Mn}^{3+}$  causing Jahn-Teller distortion [17]. Polyanion-type systems, many of which can be formulated as  $\text{LiMPO}_4$  (M refers to metal), have also been developed but are still not commercialized due to their low specific energy, low electrical conductivity and difficult synthesis procedures [18]. In addition, li-excess disordered rock salt cathode materials are also being developed and these structures form a percolated network of 0-TM channels for low potential barrier lithium ion diffusion [22]. However, short distance patterns and oxygen losses hinder the movement of lithium ions and result in capacity degradation [23]. It would be quite

appropriate to classify cobalt-free cathode materials as lithium-rich oxides, nickel rich layered oxides and lithium nickel manganese oxide (spinel structures).

Li-rich oxides have a reversible capacity exceeding  $250 \text{ mAhg}^{-1}$  and a theoretical energy density of approximately  $900 \text{ Whkg}^{-1}$ . Therefore, it stands out as an ideal cobalt-free cathode material [29]. However, phase transformations,  $\text{O}_2/\text{Li}_2\text{O}$  formation, interface problems and dissolution of transition metals are the biggest problems of this type of batteries. Due to all these problems, voltage drop, capacity decrease and slow charge/discharge rates can be experienced [33]. Ni-rich layered oxide cathodes, on the other hand, have attracted a lot of attention, but they are problematic due to structural and safety issues [34]. These problems include Ni/Li mixing, residual lithium compounds (RLC), irreversible phase transformations, transition metal dissolution and many related issues. Spinel LNMO theoretically has a specific capacity of  $146.7 \text{ mAhg}^{-1}$  and a high operating potential of  $4.7 \text{ V}$  [40]. However, the side reactions between LNMO and electrolyte at the interface are quite violent at high voltage and high temperature [41]. Moreover, the side reaction products disrupt the SEI structure on the anode surface and deplete lithium ions, resulting in degraded performance [42]. In some cases,  $\text{Mn}^{3+}$  ions in the relatively unstable LNMO (spinel) structure can be transformed into  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  ions [42], resulting in reduced cycle life. Cobalt-free cathode materials can be improved by improvements such as doping or surface coating and should be considered as Li-rich oxide, Ni-rich layered oxides and LNMO (spinel) as cobalt-free cathode materials.

## 2.1 The Role of Cobalt in Cobalt-Containing Cathode Materials

Strong electrical correlation and polaronic effects on the  $\text{LiCoO}_2$  cathode are caused by the intermediate oxidation state of cobalt, which creates an itinerant electron system [53]. Through charge delocalization, this itinerant system improves conductivity, and this may be the primary mechanism to increase the rate performance of layered oxide cathodes containing cobalt. Cobalt ions subsequently take part in the oxidation process of nickel ions, with nickel ions oxidizing earlier than other elements [54].  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NMC-111) contains  $\text{Mn}^{4+}$ , which enhances the material's thermal and electrochemical stability but has no electrochemical activity [56]. In addition to promoting electron conductivity,  $\text{Co}^{3+}$  prevents mixing of  $\text{Ni}^{2+}$  and  $\text{Li}^+$  [57]. Since nickel is the catalyst for redox processes,  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC-811) rather than

$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC-622) of NMC-111 began to be commercialized in order to achieve a greater capacity [58,59]. On the other hand, several issues pertaining to battery safety and cycling arose as the Ni concentration increased [60]. Anisotropic lattice volume variations brought on by a high degree of lithium removal at cathodes with high nickel content might mechanically harm the particles. As the Ni concentration rises, so do the levels of moisture sensitivity, Ni/Li mixing, side reactions, and phase transitions between  $\text{Ni}^{4+}$  and the electrolyte solvent [58].

Using  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$  (NCA), other cathode material, in a pouch cell produced an excellent energy density of  $160 \text{ Wh kg}^{-1}$  [61]. Because of the compound's low average valence of Ni ions, Al doping stabilized the impedance from charge transfer on the cathode side, successfully preventing the increase in battery impedance [62]. The  $\text{Ni}^{3+}$  arrangement in the LNO structure results in aligned spins, which drive an unstable, higher energy state. Since  $\text{Li}^+$  is spinless, magnetic frustration is reduced when Li<sup>+</sup> substitutes  $\text{Ni}^{3+}$  [65]. However, the process proceeds with a mixture of Ni and Li, causing the cathode lattice to be disrupted [66]. Due to the non-magnetic nature of  $\text{Co}^{3+}$ , a stable cathode is produced when Co is added to the transition metal layer, eliminating any magnetic frustration. The spins of magnetic  $\text{Mn}^{4+}$  enhance magnetic frustration while  $\text{Mn}^{4+}$  replaces  $\text{Co}^{3+}$ . According to He et al. [73],  $\text{LiNi}_{0.65}\text{Co}_{0.15}\text{Mn}_{0.2}\text{O}_2$  has a  $\text{Li}^+$  diffusion coefficient 1.42 times greater than  $\text{LiNi}_{0.7}\text{Co}_{0.1}\text{Mn}_{0.2}\text{O}_2$ . Practically speaking, since electric cars require batteries with acceptable charging performance, at least 10% cobalt is thought to be required to increase the speed performance of LIBs [74]. As expected, the rate capability may deteriorate and the Ni/Li mixing condition might be more problematic for Ni-rich layered oxides lacking Co [70, 75]. To put it briefly, Co helps provide stable cycling performance and strong rate capability for cathodes in Ni-rich layered oxides [71]. Nonetheless, with low-Co, Ni-rich layered oxides, Co has a negligible impact on cycling performance while still improving the cathode rate performance [0]. Three possible compositions with the same quantity of TM were specifically investigated by Boivin et al. [85] in order to gain a better understanding the impact of Ni and Co on the stability of the structure of Li-rich cathode materials. It was determined by this investigation that Co has no benefit when it comes to preventing the development of oxygen. Additionally, it was reported that the capacities and operating voltages decreased significantly with a decrease in temperature, while the capacity fading rates

decreased with increasing Co content in the study on the influence of tiny quantities of Co adding on  $\text{Li}_{1.2}\text{Ni}_{0.2-x}\text{Co}_{2x}\text{Mn}_{0.6-x}\text{O}_2$  ( $x = 0-0.05$ ) at low temperatures ( $-20\text{ }^{\circ}\text{C}$ ) [86].

In a similar investigation, it was shown that the  $\text{Li}_2\text{MnO}_3$  component's presence of  $\text{Co}^{3+}$  ions can enhance the component's electrochemical activation and boost its capacity in comparison to the Co-free compound [87]. Furthermore, a study conducted involved the synthesis of composite particles featuring a core-shell structure, which consists of a Co-free Mn-rich particle core surrounded by a Co-containing shell. The first cycle discharge capacity of the composite materials was greater than that of the core and shell [88]. Co doping generally has a limited impact and is unable to address the underlying issues with lithium-rich materials, however it can somewhat enhance the low-temperature performance and capacity of Li-rich oxide cathodes. The influence of cobalt in the structure is evident in cobalt-modified LNMO; nevertheless, it is thought that alternative coating layers of fast, Co-free  $\text{Li}^+$  conductors have the similar effect. As a result, it is not thought that cobalt needs to be used specifically [0].

## 2.2 Cobalt-Containing Cathode Materials

Layered metal oxide cathode materials can typically be formulated as  $\text{LiMO}_2$  ( $\text{M}$ =transition metal or metals) and each has an  $\alpha\text{-NaFeO}_2$  phase structure. In these materials,  $\text{MO}_6$  and  $\text{LiO}_6$  have a crystal structure consisting of successive arrays of octahedral structures, where oxygen atoms occupy the FCC structure and transition metal(s) occupy the vacancies in the octahedral structure.

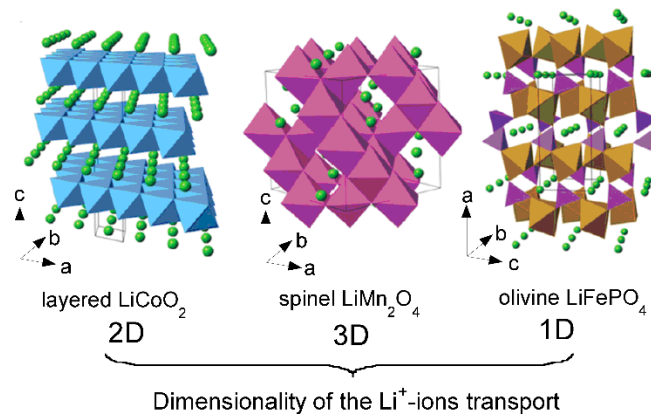
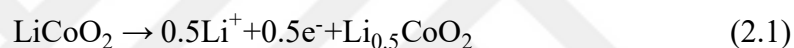


**Figure 2.2:** Schematic view of lithium ion transportation in main cathode materials having different crystal structures [32].

Lithium ions are located between oxygen atoms. Thanks to its crystallography, these structures have the ability to accommodate a large number of atoms in layered, two-

dimensional interstitial spaces and provide diffusion [31]. Lithium ion transport in different crystal structures is shown in Figure 2.2.

LCO was the first cathode to be commercialised in this type of cathode materials. It is a cathode material that is still used today when it has features such as high discharge potential, energy density, superior cycling performance and easy synthesis. Thanks to the layered structure, the edge-sharing  $\text{CoO}_6$  octahedral structures in LCO, which make the diffusion of lithium ion fast, also enable direct Co-Co sharing, providing very good electronic conductivity and thus showing a remarkable rate capability. Apart from this, the  $\text{Co}^{3+/4+}$  redox reaction offers a high potential value of 4V towards lithium [33]. LCO has a theoretical specific capacity of 274 mAhg<sup>-1</sup> with all lithium removed from the structure. However, in practice, Li/Li<sup>+</sup> shows only 140 mAhg<sup>-1</sup> specific capacity in the range of 3-4.2 V. This is because the lithium ions separated from the main structure are about half of the total lithium ions [34]. This can be shown by the following equation.



Charging LCO batteries above 4.2 V is quite risky due to safety issues. The reason for this is the loss of oxygen in the structure in high voltage situations due to the overlap of the  $\text{Co}^{3+/4+}$  3d band with the upper part of the  $\text{O}^{2-}$  p band and the oxidation of  $\text{O}^{2-}$  ions on the surface to  $\text{O}_2^{2-}$  with the removal of more lithium ions from the structure. Due to the low practical capacity of LCO, various coatings and methods are applied to improve material conductivity, physical structure and to prevent reactions between electrolyte and electrode. In addition, doping can also be applied as another method. The high cost and toxicity of LCO have also led researchers to alternative cathode materials such as  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$ ,  $\text{LiFeO}_2$  (see Table 2.1).

**Table 2.1:** Some layered, spinel and olivine structures and their electrochemical properties [32].

| Structural type | Cathode material          | Specific capacity (mA h g <sup>-1</sup> ) |           | Average discharge voltage vs Li <sup>+</sup> /Li(V) |
|-----------------|---------------------------|-------------------------------------------|-----------|-----------------------------------------------------|
|                 |                           | Theoretical                               | Practical |                                                     |
| Layered         | $\text{LiCoO}_2$          | 274                                       | 140       | 3.9                                                 |
|                 | NCA                       | 280                                       | 160       | 3.8                                                 |
|                 | NMC 111                   | 275                                       | 160       | 3.8                                                 |
|                 | NMC 811                   | 275                                       | 200       | 3.8                                                 |
| Spinel          | $\text{LiMn}_2\text{O}_4$ | 148                                       | 120       | 4.0                                                 |
| Olivine         | $\text{LiFePO}_4$         | 170                                       | 150       | 3.5                                                 |

LiNiO<sub>2</sub> is one of the cathode materials with a similar structure to LCO. LNO, which has a theoretical capacity of 275 mAhg<sup>-1</sup> and an operating voltage range of more than 3.7 V, is highly advantageous in terms of cost, less toxic and higher reversible capacity compared to LCO. In LNO, the Ni<sup>3+/4+</sup> 3d bands overlap only the upper part of the O<sup>2-</sup> p band before oxygen loss. Therefore, most of the lithium in the structure can leave the structure and can reach high capacity values such as 200 mAhg<sup>-1</sup>. One of the biggest problems of this material is that LNO cannot be produced stoichiometrically and the synthesised materials are always obtained as Li<sub>1-y</sub>Ni<sub>1+y</sub>O<sub>2</sub>. This is due to the mixture of Li<sup>+</sup> (0.76 Å) and Ni<sup>2+</sup> (0.69 Å) [35]. Intercalation of the lithium ion occurs when it moves from the octohedral site to the tetrahedral site and then back to the other octohedral site. Usually nickel atoms in tetrahedral structures are shared by the edge of only one nickel atom. When the structure is disordered, this number may increase to two or three. The high charge amount of nickel creates strong electrostatic repulsion on lithium ions. However, Kang et al. stated that the changes made in the plate-like region where lithium ions are located are more dominant than electrostatic repulsion. In structurally disordered material, the narrowing of these regions makes diffusion more difficult, resulting in lower capacity and velocity capability [36]. Its commercial usage is quite limited since the synthesis processes also need severe temperature conditions. Furthermore, low thermal stability and capacity loss during cycle are issues that LNO exhibits. The +4 valence of nickel is the primary cause of the poor thermal stability, and the capacity loss is strongly influenced by the synthesis technique. Oxygen formation occurs at high temperatures due to the instability of the LiNiO<sub>2</sub> structure, causing safety and security problems [37]. Due to these problems, LNO could not compete with LCO.

Layered LiMnO<sub>2</sub> has been investigated in detail as an alternative cathode material in terms of being environmentally safe and low cost. LMO shows a very high capacity of 270 mAhg<sup>-1</sup> under 4.3 V. In general, LMO can be monoclinic (layered, C2/m) and orthorhombic (zigzag layered, Pmmn), which is thermodynamically more stable. However, the similarity in diameter of the lithium ion and the Mn<sup>3+</sup> (0.65 Å) ion prevents the LMO from having a stable structure. Thus, the structure is thermodynamically unstable and has poor electrochemical performance [38]. During charging, LiMnO<sub>2</sub> transforms into a more stable phase, spinel LiMn<sub>2</sub>O<sub>4</sub>. This is due to the presence of low spin Mn<sup>3+</sup> ion (Jahn-Teller ion). Therefore, a capacity decrease is

observed during cycling. However, this phase transformation can create an advantageous situation due to the same oxygen network of both  $\text{O}_3\text{-LiMnO}_2$  and  $\text{LiMn}_2\text{O}_4$ , which can provide easy diffusion of cationic species. The contact between the LMO and the electrolyte can generate the reaction  $2\text{Mn}^{+3} \rightarrow \text{Mn}^{+2} + \text{Mn}^{+4}$ , and the formed  $\text{Mn}^{2+}$  can diffuse from the manganese layer to the lithium layer. Studies show that crystal structures can be stabilised by the substitution of manganese with low valence metal ions [39].

$\text{LiFeO}_2$  is another layered cathode material. It has a rock-salt structure similar to LCO, has a theoretical capacity of  $282 \text{ mAhg}^{-1}$  and has attracted a lot of attention with its non-toxicity.  $\text{LiFeO}_2$  can be found in many types such as  $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{LiFeO}_2$ , hollandite. Among them,  $\alpha$ - $\text{LiFeO}_2$  is electrochemically active with its disordered rock salt structure, is very easy to synthesise and has remarkable electrochemical properties [40]. However, poor electronic conductivity and slow diffusion of lithium ions considerably reduce the rate capability and cycling properties. In order to overcome these problems, particle size reduction, carbon coating and ion doping have been carried out. 1D nanostructured materials such as nanorods, nanowires, nanotubes facilitate lithium storage properties and transport.

When looking at chemically rich cathode materials as layered oxide structures, many elements have been added to  $\text{LiMO}_2$  based metal oxides in order to provide good electrochemical properties and stability. Materials with  $\alpha$ - $\text{NaFeO}_2$  structure, in which transition metals do not enter the lithium layers, show excellent electrochemical properties. The stability of these layered oxide structures is generally dependent on the size of the transition metals compared to alkali metals. Manganese-added binary solid solutions can have discharge capacities as high as  $200 \text{ mAhg}^{-1}$  as they show high thermal stability due to the suppression of exothermic reactions by manganese. It also ensures the structural stability of the material during cycling as the  $\text{Mn}^{4+}$  ion creates a hindrance to cationic movement between layers. However, this leads to Li/Ni mixing with an equal amount of  $\text{Ni}^{3+}$  ions converting to  $\text{Ni}^{2+}$  in order to achieve charge balance [41]. In binary solid solutions, charge/discharge occurs in the range of 3.6-4.3 V and  $\text{Ni}^{2+}/\text{Ni}^{4+}$  2-electron reduction occurs in this voltage range.  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  material in nickel-rich  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  phase has a similar structure to LCO and LNO and has a stable specific capacity value of  $180 \text{ mAhg}^{-1}$ . Without oxygen loss, 65% of the lithium ions can be reversibly in and out of the structure during charging and

discharging. The Jahn-Teller distortion caused by the presence of  $\text{Ni}^{3+}$  can be alleviated by the addition of cobalt. With the addition of cobalt, the structural strain in  $\text{NiO}_6$  octahedra positions decreases and the electrode resistance decreases. Therefore, sustainable capacity values can be achieved in the  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  structure and high thermal stability can be achieved due to the strong Co-O bond. The one-electron reduction reaction  $\text{Ni}^{3+}/\text{Ni}^{4+}$  generally takes place in these solid solutions [42]. Aluminium doping into the  $\text{LiNiO}_2$  structure prevents the formation of undesired phases and adds thermal stability and good cyclic properties. However, the electrochemical inactivity of aluminium should be minimised in the  $\text{LiNiO}_2$  structure [43].

Recently, nickel-rich cathode materials have become suitable for use in electric vehicles due to their low cost, high capacity and less toxicity. The addition of  $\text{Co}^{3+}$  to  $\text{Ni}^{3+}$  has been widely studied to prevent the conversion of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  and its entry into lithium layers.  $\text{Co}^{3+}$  reduces  $\text{Ni}^{2+}$  formation and contributes to the formation of  $\text{Li}(\text{Ni},\text{Co})\text{O}_2$  solid solution since its diameter (0.545 Å) is very close to  $\text{Ni}^{3+}$  (0.56 Å) [44].  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) is used in Tesla's electric vehicles. This is because it shows superior capacity values and is cheaper than LCO. NCA theoretically has a capacity of  $280 \text{ mAhg}^{-1}$  and studies show that it gives higher capacity values such as  $199 \text{ mAhg}^{-1}$  than materials such as LCO and LFP. However, NCA shows low initial efficiency, capacity decrease and low reversible capacity due to cationic mixture, microcracks in particles and formation of NiO-like phases. Furthermore, as the nickel content increases, reactions with moisture and  $\text{CO}_2$  can develop rapidly, resulting in the formation of  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$  on the cathode surface. During the cycle, a high amount of oxidised  $\text{Ni}^{4+}$  reacts with the electrolyte and deterioration of electrochemical performance occurs [45].

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC-111) has high operating potential values such as 4.7 V. It can reach capacity values of  $160 \text{ mAhg}^{-1}$  in the 2.4-4.4 V potential range and  $200 \text{ mAhg}^{-1}$  in the 2.8-4.6 V potential range [46]. It also shows very good rate capacity of  $150 \text{ mAhg}^{-1}$  at  $1600 \text{ mA g}^{-1}$  and very good structural stability at high potential values [47]. This makes NMC 811 very interesting. During charging, the valence of nickel is raised from +2 to +4, while that of cobalt is raised from +3 to +4. The valence of manganese remains constant at +4 during this process [48]. During the charging process, a decrease in the Fermi level of the main structure occurs. In the case of a

high amount of lithium leaving the structure, the Fermi level is located just above the O(2p) band, providing an intrinsic voltage limit for NMC-111 [49]. In Figure 2.3, NMC structure was shown schematically.

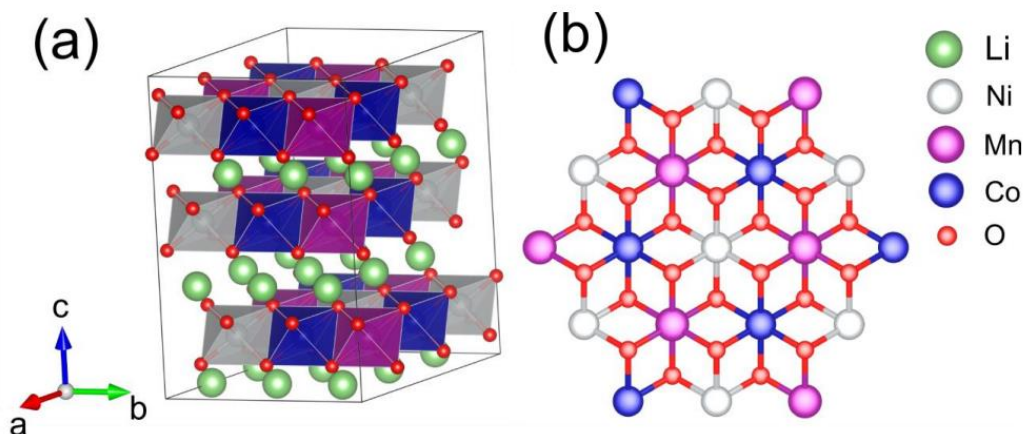


**Figure 2.3:** Schematic representation a) in bulk structure b) ion ordering for NMC-811 [50].

$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811) are the cathode materials under investigation in this cathode family and have a capacity of  $200 \text{ mAhg}^{-1}$  between 3-4.3 V. Nickel content is higher than manganese in these cathode materials. It is quite similar to  $\text{LiNiO}_2$  structures in terms of electrochemical behaviour and the fact that all nickel is apparently  $+3$  valence. This type of material usually has problems with capacity conservation due to the instability of  $\text{Ni}^{4+}$  ions. When the structures of NMC-622 and NMC-532, which are other NMC materials, are examined, it is reported that cobalt is responsible for the rate capacity, nickel for the capacity and manganese for the thermal stability. However, high nickel content creates a problem in capacity fade due to instability in the structure during cycling. This problem can be overcome by using low valence transition metal ions. Although the incorporation of cobalt in the structure increases the cost, it reduces the Li/Ni mixture and thus increases the rate capability and eliminates the safety issues related to NMC [51]. Comparisons between NMC cathodes according to their composition was shown in Figure 2.4.

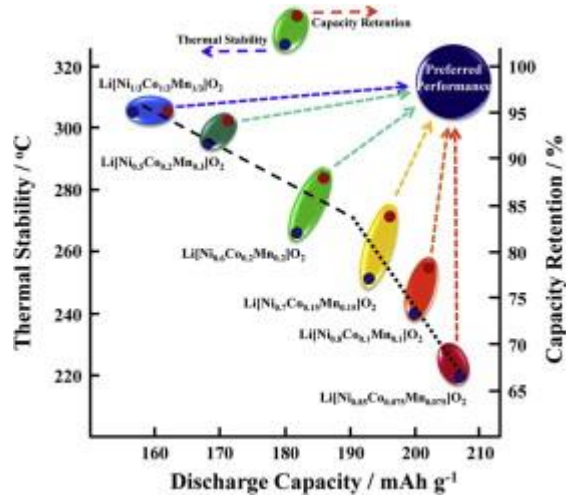


**Figure 2.4:** Connection among NMC materials' discharge capacity (black), thermal stability (blue) and capacity retention (red) [51].

## 2.3 Cobalt-Free Cathode Materials

### 2.3.1 Li-rich oxide structures

Lithium-rich cathode materials can theoretically reach  $460 \text{ mAhg}^{-1}$  capacity values. However, because of their structural deterioration and adverse reactions caused by the reactions between the cathode and the electrolyte during the first cycle, they show capacity values around  $250 \text{ mAhg}^{-1}$ . Oxygen evolves to make up for the decreased positive charge when the lithium ion is totally eliminated from the structure. This causes the oxygen-bonded manganese to become unstable and the phase structure to change from layered to spinel [52], [53]. This process can take place in 6 steps. In the first step, when charging starts at 3.2 V, lithium ions start to exit from the octahedral (3b) regions and vacancies are created in the lithium layer. With the increase of lithium vacancies around 4.1 V in the second step, lithium ions in octahedral regions migrate to tetrahedral regions in the lithium layer. In the third step, lithium ions in the layer of octahedral transition metals also migrate to tetrahedral sites and a phase structure is formed in the form of a transition from layered to spinel structure. In the fourth step, at a charge potential above 4.1 V, manganese in the octahedral region with transition metal ions jumps through oxygen vacancies to the tetrahedral regions in the lithium layer. In the fifth step, during charging above 4.5 V, the manganese ions migrate to the octahedral region in the lithium layer. In the last step, the sixth step, during the charge-discharge cycle, these atomic arrays undergo a structural change from a layered structure to a spinel structure. When enough vacancies are created in the lithium layer, the lithium ion can move from the octahedral sites in the TM layer to the tetrahedral

structure in the lithium layer [54], [55]. As a result, this makes it difficult for lithium to enter and exit the structure, resulting in low rate performance and significantly lower capacity. In Figure 2.5, conversion from layered to spinel structure was shown.

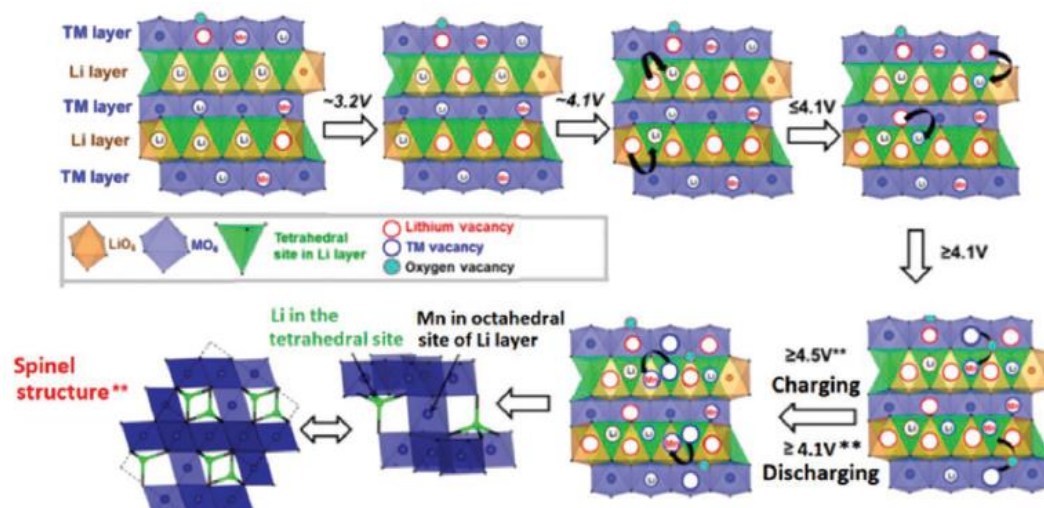


**Figure 2.5:** Phase transitions process from layered to spinel structure [55].

Besides the structural change, a series of electrochemical reactions also occur. According to Equation 1, when the potential value is less than 4.4 V, the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  is observed in the delithiation process. According to Equations 2-4, when the potential value is above 4.4 V,  $\text{Li}^+$  and oxygen are removed from the system with the formation of  $\text{O}_2$  or  $\text{Li}_2\text{O}$  [52], [56]. The released oxygen reacts with the electrolyte and forms unwanted products.  $\text{Li}_2\text{O}$  can then react with these by-products to form water. As a result, lithium hydroxide may be formed [57], [58]. Large changes in pH at the end of discharge cause loss of active material, resulting in precipitation in the form of  $\text{Li}_2\text{CO}_3$  and poor performance.

In addition to the capacity drop, another problem is the voltage drop due to the reduction of manganese and cobalt. Long cycles result in an increase in capacity due to  $\text{Mn}^{3+}/\text{Mn}^{4+}$ . Based on the OCV, which depends on the Fermi level energy, the Fermi level is initially above  $\text{Ni}^{2+}/\text{Ni}^{3+}$ . However, during the first cycle, reduction of manganese may occur due to oxygen losses, raising the Fermi level and lowering the operating voltage [59]. Subsequently, the weakened bond between TM and oxygen may remove oxygen anions from the crystal structure in subsequent charge-discharge cycles [60]. In summary, lithium-rich cathode materials suffer from three main problems: voltage instability, capacity drop and slow charge/discharge. The biggest obstacle to the industrialization of lithium-rich oxide materials is severe voltage drop.

### 2.3.2 Spinel and olivine structures

LNMO cathode material is unique in that it can be used in all solid-state 5 V Li-metal batteries because of its high voltage working values [61]. When combined with an LTO anode, it has a voltage range of 3.2 V and provides safety and high power output as well to its high working voltage [62]. It also has a 3D spinel lattice structure that enables fast movement of lithium ions. According to a published study, it shows a stable structure up to 40°C charge-discharge rate [63]. It has ordered or disordered crystal arrangement according to crystal structure. This crystal structure varies according to the calcination temperature. For example, as a result of calcination below 700°C, LNMO has a simple cubic structure and has an ordered structure. This indicates that nickel, manganese and lithium are located in specific places in the crystal structure. In the disordered or face-centered cubic structure, nickel and manganese are randomly distributed in octahedral regions [64]. Annealing at high temperatures causes oxygen and nickel deprivation in the structure, resulting in the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  due to charge equilibrium [65]. Disordered LNMO shows solid-solution reaction and phase transformation involving  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Ni}^{3+}/\text{Ni}^{4+}$  redox pairs [66]. However,  $\text{Mn}^{3+}$  then decomposes into  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$ .  $\text{Mn}^{2+}$  can dissolve in the electrolyte and migrate to the anode causing anode degradation [67]. Disordered LNMO is known to have higher electronic conductivity at low SOC level. However, it shows very similar values with ordered structure in terms of conductivity in fully charged state [68].

Side reactions such as transition metal dissolution, self-discharge, HF formation can occur at the LNMO and electrolyte interface. In the system where  $\text{LiPF}_6$  is generally used as electrolyte,  $\text{LiPF}_6$  in carbonate can oxidize around 4.5 V [69]. In this case, by-products such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{POF}_3$  and  $\text{C}_2\text{H}_5\text{OCOO}\text{PF}_4$  may be formed. These by-products react with the lithium ions forming the ECI and SEI film and lead to a decrease in capacity. In fact,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  transition metals are formed due to side reactions between the electrolyte and  $\gamma\text{-MnO}_2$  regardless of the difference in crystal structure [70]. In addition, a small amount of  $\text{Mn}^{3+}$  ions are present in the disordered structure due to the disproportionation of  $\text{Mn}^{2+}$  [67]. The dissolved  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  ions migrate to the anode and can reduce the SEI film. This causes the electronic conductivity of the anode to drop drastically, greatly reducing the number of recoverable lithium ions in the full cell structure [67], [71]. Dissolved transition metal

ions disrupt the SEI by displacing the lithium ions in the SEI and adversely affect the cycling performance of the battery [71]. These side reactions result in internal resistance and loss of recoverable lithium. The effect of transition metal ions in the half-cell on the loss of recoverable lithium is very small, less than 5% [67]. This is indicative of the stability of the LNMO in the half-cell, although significant side reactions occur throughout the cycle.

The bulk stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is acceptable, but serious interfacial problems are encountered, especially at high voltage values. For this reason, studies on surface modification, electrolyte and electrolyte additive are being carried out. Especially gel polymer electrolyte not only prevents  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  migration but also promotes corrosion reactions due to  $\text{LiPF}_6$  in the limited liquid electrolyte in the gel polymer electrode. Spinel LNMO is extremely important for 5V Li-metal batteries, but the problems between the electrolyte/solid interface are still to be solved. In the commercialization phase, there are still problems at the level of material selection rather than electrolyte selection and cell design. The primary problem is to produce LNMO at low cost without causing environmental problems. The interfacial problems are relatively easy to solve because the LNMO (spinel) cathode does not undergo volume change. This means that the interface cannot be constantly changed and consumed. Therefore, LNMO (spinel) as a cathode needs further research.

Compared to other cathode materials,  $\text{LiFePO}_4$  has several benefits, including a flat voltage profile, inexpensive price, abundant supply of resources, and environmental friendliness.  $\text{LiFePO}_4$  does, however, also have comparatively low theoretical capacity, low density, poor electrical conductivity, and low ion diffusion in addition to these benefits. Furthermore, the production cost of LFP is considerable since it needs a carbon coating or tiny particle sizes to work well at high currents [72]. The following Table 2.2 shows how LFP compares to different cathode materials.

One of the original battery types for electric cars was LFP. These are the thresholds that need to be surpassed, according to the US Department of Energy, in order to commercialize high-energy batteries for use in plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs) (see Table 2.3). These limits; These are limits for battery performance, cost, lifespan and problems that may arise in adverse conditions [72].

**Table 2.2:** Comparing the characteristics of several cathodes in 18650 batteries [73].

| Property                               | LiAl <sub>0.05</sub> Co <sub>0.15</sub> Ni <sub>0.8</sub> O <sub>2</sub> | LiCoO <sub>2</sub> | LiMnO | LiFePO <sub>4</sub> |
|----------------------------------------|--------------------------------------------------------------------------|--------------------|-------|---------------------|
| Avg. voltage (V)                       | 3.65                                                                     | 3.84               | 3.86  | 3.22                |
| Theo. capacity (mAhg <sup>-1</sup> )   | 265                                                                      | 274                | 117   | 170                 |
| True density (g cm <sup>-3</sup> )     | 4.73                                                                     | 5.05               | 4.15  | 3.60                |
| Specific energy (Wh kg <sup>-1</sup> ) | 219.8                                                                    | 193.3              | 154.3 | 162.9               |
| Energy density (Wh L <sup>-1</sup> )   | 598.9                                                                    | 557.8              | 418.6 | 415.0               |
| Materials cost                         | 1.628                                                                    | 1.824              | 1.159 | 1.219               |
| Energy cost (Wh US\$ <sup>-1</sup> )   | 6.08                                                                     | 5.05               | 5.97  | 6.31                |

**Table 2.3:** An overview of the main specs for PHEV and HEV batteries [72].

| Characteristics                                  | HEV        | PHEV (10 Miles) | PHEV (40 Miles) |
|--------------------------------------------------|------------|-----------------|-----------------|
| Pulse discharge power (kW 10s <sup>-1</sup> )    | 300,000    | 38              | 46              |
| Available energy (kWh)                           | N/A        | 3.4             | 11.6            |
| Cycle life (charge sustaining, 50 Wh)            | 300,000    | 300,000         | 300,000         |
| Cycle life (charge depleting)                    | N/A        | 5000            | 5000            |
| Calendar life (years)                            | 15         | 15 (35°C)       | 15 (35°C)       |
| Maximum weight (kg)                              | 40-60      | 60              | 120             |
| Maximum volume (L)                               | 32-45      | 40              | 80              |
| Max. price (\$) (100k units year <sup>-1</sup> ) | 500-800    | 1700            | 3400            |
| Operating temperature (°C)                       | -30 to +52 | 0 to +52        | -30 to +52      |

LiFePO<sub>4</sub> is an orthorhombic lattice structure lithium ortho-phosphate that is a member of the olivine family in the Pnma space group (Figure 2.6). Lattice parameters are a = 10.33 Å, b = 6.01 Å, c = 4.69 Å and volume is 291.2 Å<sup>3</sup>. LiFePO<sub>4</sub> has a corner-sharing octohedral FeO<sub>6</sub> structure connected to each other by the PO<sub>4</sub> tetradral structure and an edge-sharing LiO<sub>6</sub> structure parallel to the b axis. Sharing types was shown in Figure 2.7. Lithium is removed from the structure without disrupting the olivine structure, resulting in heterocytic FePO<sub>4</sub>. However, in this case, the lattice parameters change to a = 9.81 Å, b = 5.79 Å, c = 4.78 Å and the volume is 271.5 Å<sup>3</sup>. This results in a 6.77% decrease in volume, a 5% and 3.7% decrease in the a and b lattices, respectively, while a 1.9% increase in the c lattice [74].

Compared to layered oxide structures like LiCoO<sub>2</sub>, which is stable up to 250 degrees, LFP, which is stable up to 400 degrees, has far greater endurance at high temperatures because oxygen atoms are firmly bound to the iron and phosphate structure [75], [76]. This lattice stability also causes the cycle performance and LFP to be a safe cathode material. Unfortunately, strong covalent oxygen bonds also cause low ion diffusion and low electrical conductivity [76]. It is widely believed that the diffusion of lithium is unidirectional along the b-axis [77]

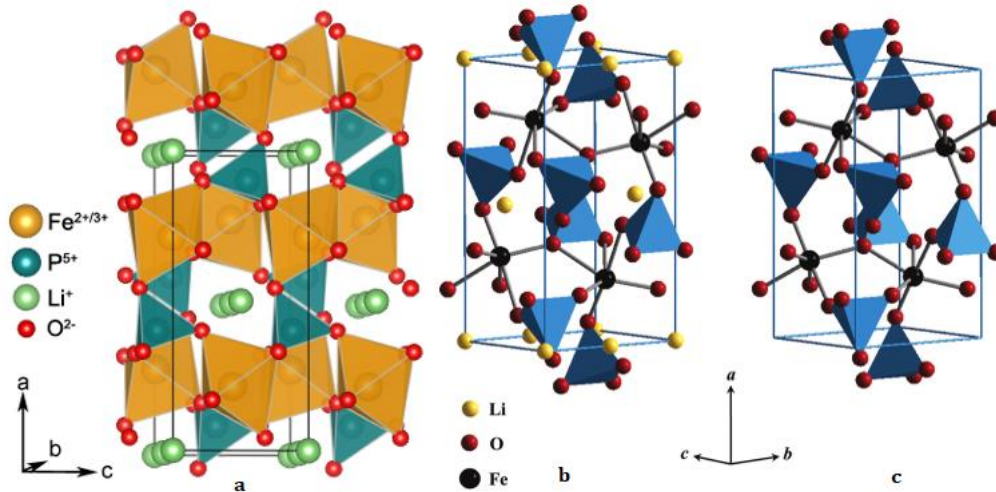


**Figure 2.6:** Crystal structure of a,b)  $\text{LiFePO}_4$  c)  $\text{FePO}_4$  [78].

It is known that the driving force of diffusion is the concentration difference. Increasing the concentration difference causes faster diffusion. However, since both  $\text{LiFePO}_4$  and  $\text{FePO}_4$  have a low solid solution formation range, it is not possible for them to have a high concentration difference and therefore high lithium diffusion [79]. For particles bigger than 100 nm, solubility at room temperature is thought to be less than 0.05, and at higher temperatures the miscibility range falls between these two phases [80], [81].

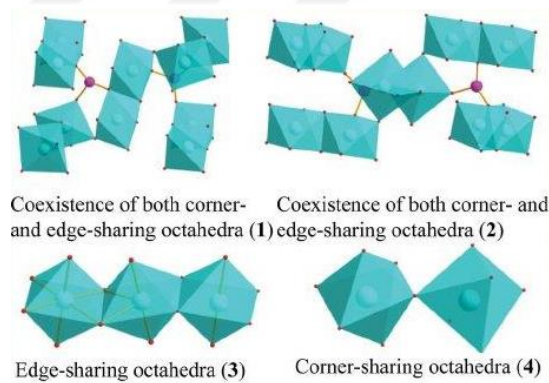


**Figure 2.7:** Corner and edge-shared structures [82].

Around  $200^\circ\text{C}$  is when  $\text{Li}_x\text{FePO}_4$  changes from a heterocytic and triphylite structure to a disordered solid solution (shown in Figure 2.8). Above  $300^\circ\text{C}$  these two phases totally dissolve. It should be mentioned that the surface energy effect causes the phase diagram to be heavily influenced by particle size [81]. It is projected that a complete solid solution will occur at room temperature and that a complete solid solution will occur when the particles have a size of 15 nm. The miscibility ratio between  $\text{LiFePO}_4$  and  $\text{FePO}_4$  diminishes as the particle size is lowered below 50 nm [83].

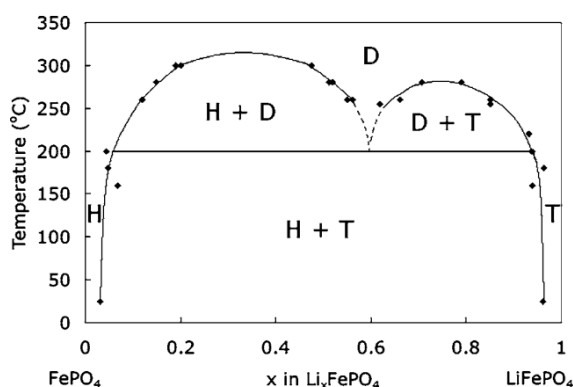


**Figure 2.8:** Phase diagram of the LiFePO<sub>4</sub> (T) and FePO<sub>4</sub> (H) phases in a eutectoid system, illustrating their connection into a solid solution (D) for disordered. Around 200°C and a composition of  $x = 0.6$  is where the eutectoid region is located. Heterosite or triphylite and disordered phase combinations have been detected over 200°C and have reached 300°C. The disordered phase predominates at 300°C [80].

The core-shell concept, also known as the mosaic model, was initially proposed as the method via which lithium penetrates and departs the structure [84]. These ideas suggested that the shell was created by one phase and the core by another. Diffusion happened because of the interface's mobility across the shell. These ideas have been called into doubt by the discoveries that multiple FePO<sub>4</sub> areas are present in LiFePO<sub>4</sub> particles, where lithium is partially extracted from the structure, and that the interface regions are not a solid solution but rather a superposition of two terminal phases [85]. These discoveries led to the development of the spinodal-decomposition model [85] and the domino-cascade model [86]. According to both models, phase boundaries change to allow Li ions to co-move along b-channels during both entering and leaving processes (in front of nucleation). Solid solution zones are not required because the process is not diffusion controlled in origin .

These two models confirm that the grain boundary governs the one-dimensional phase transition kinetics [87]. However, the main difference among both of these models is the movement rate of the grain boundaries. According to the domino-cascade model, each particle is either a single triplith or a single heterocyte, and no particles with mixed phases are detected during the reaction process due to the incredibly rate of change. Particles where lithium leaves the structure seem to have several domains and phase interfaces, and phase boundaries appear to be a little slow, according to the spinodal-decomposition model [86]. Depending on surface coating, synthesis method, particle size, charging rate, and testing protocols, lithium moves through and out of

structures in various ways [88]. Mechanisms are schematically demonstrated in Figure 2.9.

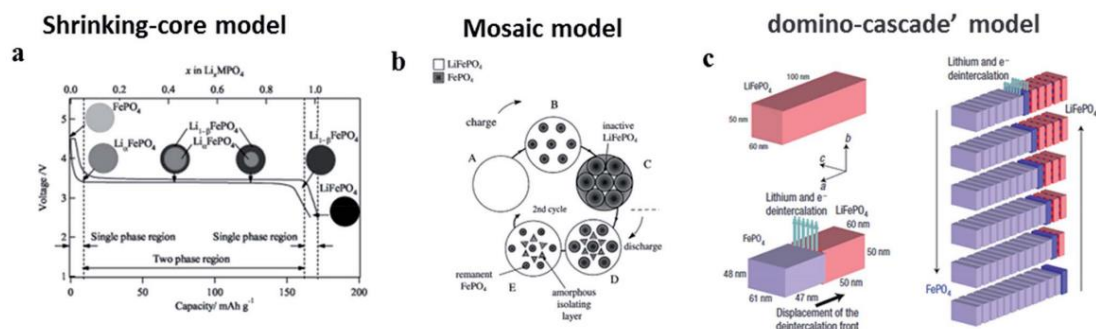


**Figure 2.9:** Models of the lithium insertion and extraction mechanisms shown schematically a) Shrinkage-core model b) Mosaic model c) Domino-cascade model [89].

### 2.3.3 Ni-rich oxide structures

In early 1998,  $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$  ( $0.1 \leq x \leq 0.5$ ) systems were first synthesized and found to have better stability than LNO [90]. Ohzuku and Makimura observed that  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  has a thermal runaway problem with lower impact than  $\text{LiCoO}_2$  [91]. Kang et al. also synthesized the same cathode with much less interlayer distortion, resulting in higher C-rate performance [92]. With the addition of manganese to the structure, the cathode shows better thermal stability, while the capacity increases with increasing nickel content [93]. As the manganese content increases, the capacity retention property also improves due to chemical and structural stability. Capacity values increase with increasing nickel content in these systems, while capacity decreases with increasing manganese content. The reason for this is that increasing manganese content creates a kinetic barrier in the lithium layers of  $\text{Ni}^{2+}$  ions [94]. Liu et al. studied a cobalt-free  $\text{LiNiMnXO}_2$  ( $X = \text{one or more dopants}$ ) system and found that cobalt suppresses the Li/Ni mixture to a large extent but leads to more severe morphological and structural distortions during cycling. Examples include dissolution of transition metals and oxygen release [95]. More manganese substitution in the structure leads to a higher amount of Li/Ni mixing but better stability of the bulk structure [96]. Layered oxide structures rich in nickel content face many problems affecting material stability and safety at high voltages and/or elevated temperatures, especially in charging or storage [97]. These include Ni/Li mixing, residual lithium compounds (RLCs), phase transformations, oxygen release, reactions with the electrolyte, dissolution of transition metals and crack formation within the particle.

Ni/Li mixing is the most common and major problem encountered in nickel-rich layered oxide structures. This problem, which increases with increasing nickel content, can occur not only during synthesis but also during charging and discharging [98]. In this problem, nickel is located as  $\text{Ni}^{2+}$  in the layer of lithium atoms. This is due to the similar diameter size of  $\text{Ni}^{2+}$  ions and lithium atoms, as well as the low migration barrier for  $\text{Ni}^{2+}$  ions to migrate into lithium layers [99]. Zheng et al. list three main reasons for this problem. These are the steric interaction based on the relaxation mechanism of  $\alpha\text{-NaFeO}_2$  and  $\alpha\text{-LiFeO}_2$  structures being the driving force for this problem, the superexchange of the strong linear  $\text{Ni}^{2+} - \text{O}_2 - \text{Ni}^{2+}/\text{Mn}^{4+}$  interlayer and the lower energy barrier for the migration of  $\text{Ni}^{2+}$ , which creates a kinetic energy advantage [100]. Cobalt addition prevents Ni/Li mixing by creating shielding effect due to magnetic frustration in the structure [101], [102]. RLCs adversely affect battery performance in terms of coulombic efficiency, cycling characteristics and storage characteristics [103]. This is highly dependent on humidity level, storage time and voltage. RLCs are present as  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$  on nickel-rich cathode structures and this can happen during the synthesis process or during cycling. Lithium ions are trapped on the particle surface as by-products [103]–[105]. Considering  $\text{Li}_{1-x}\text{NiO}_2$  in an LNO cathode system during the charging and discharging process, hexagonal (H1), monoclinic (M), hexagonal (H2) and hexagonal (H3) phase transformations occur during charging, i.e.  $0 \leq x \leq 0.25$ ,  $0.25 \leq x \leq 0.5$ ,  $0.5 \leq x \leq 0.75$  and  $0.75 \leq x \leq 1$ , respectively [106], [107]. Especially during the H2-H3 phase transformation, intergranular cracks occur as a result of long cycles. This is due to the accumulation of strains in the structure during contraction and expansion [108]. In addition, transitions from layered structure to spinel or rock salt structure due to oxygen release also create local stresses, creating microcracks and causing peeling of the particles [109]. Due to the crack in the particle, the electrolyte reacts with those areas and results in thermal runaway [110].  $\text{Ni}^{4+}$  formed during full charge is reduced to  $\text{Ni}^{3+}$  during phase transformation and  $\text{Ni}^{3+}$  is reduced to  $\text{Ni}^{2+}$  with increasing temperature [111]. This is ultimately explained by the Ni/O ratio and oxygen loss [112] and thermal runaway occurs [113], [114]. In one study, a large number of phase transformations take place on the cathode surface due to direct contact with the electrolyte, so proper isolation can prevent interfacial reactions between the electrolyte and the cathode. At the same time, phase transformations can occur at the solid/solid interface as a result of voids due to oxygen loss. These phase transformations usually occur at coherent twin boundaries, but also

occur at incoherent boundaries to a lesser extent [114]. Phase transformation causes microcracks in the particle structure, leading to gas oscillation and increasing the impedance of the battery, resulting in a decrease in discharge capacity and battery voltage. When interfacial problems are addressed, for example, when carbonate is considered, the formation of carbon oxygen gas leads to the formation of  $\text{H}_2\text{O}$  [131]. The resulting  $\text{H}_2\text{O}$  reacts with  $\text{LiPF}_6$  salt and  $\text{H}_\text{F}$  is released as a product.  $\text{HF}$  reacts with TM oxides and forms soluble  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  ions. These ions cause a loss of TM ions, which leads to a decrease in battery capacity and operating voltage. Furthermore,  $\text{Ni}^{2+}$  ions enter the lithium layers and promote phase transformations in nickel-rich cathode materials [115]. A fully charged nickel-rich cathode experiences  $\text{Ni}^{4+}/\text{Ni}^{3+}$  reduction, which promotes easy reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$ , increasing the Ni/O ratio or causing oxygen loss [113]. The fresh cathode surface tends to react with the electrolyte due to cracking and thermal runaway occurs when the electrolyte is also consumed [116].

### **2.3.3.1 Possible approaches for improvements**

#### **Doping**

In order to overcome the aforementioned problems, doping, surface modification, electrolyte additive developments and single crystal synthesis technologies come to the forefront. Doping prevents surface degradation in the electrode material and improves the performance of the battery. The reason for this is that it increases the coherence of surface oxygen in the structure. Anionic doping improves some properties and adversely affects others. Kong et al. studied F, S, Cl anions in  $\text{LiNiO}_2$  cathode and investigated the Li/Ni mixture, ionic conductivity, lattice distortion and nickel migration in the battery cell. The studies showed that fluorine could be a candidate anion with a favorable effect on all these properties. However, fluorine increases Li/Ni mixing which inhibits lithium diffusion. Chlorine and sulfur doping showed similar performances. Anionic doping additions positively affected Li/Ni mixing and lattice distortion, but there is clearly a dichotomy between structural stability and rate performance. Since the choice of the doping element and the position at which the substitution occurs are important in doping, the size, electronegativity and electron localization of the ions are very important factors [117].

$\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$ , which have multiple oxidation states or reduction potentials in the operating voltage range of the battery and enter the lithium layers, seem to be

suitable candidates [118]. The atomic position of the cation affects the strength and structural stability of the Ni-O bond quite effectively [98]. At 2.5-4.6 V range and 0.2C cycle rate, 1 mol% Cu<sup>2+</sup> doping of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathode material helped to achieve 18% higher capacity value compared to pristine structure [119]. Li et al. synthesized LiNi<sub>0.495</sub>Mn<sub>0.495</sub>Mo<sub>0.01</sub>O<sub>2</sub> cathode and reached a capacity value of 180 mAhg<sup>-1</sup>. This was obtained as 156 mAhg<sup>-1</sup> in LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathode. Based on this study, it was concluded that molybdenum inhibits Li/Ni mixing and suppresses phase transformations [120]. Similarly, LiNi<sub>0.4</sub>Mg<sub>0.1</sub>Mn<sub>0.5</sub>O<sub>2</sub> showed a discharge capacity of 188 mAhg<sup>-1</sup> at 0.1 C and in the range of 2.9-4.8 V [121]. In the LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathode with antimony doping, the capacity retention at 1C after 250 cycles was 81%, while it was only 59% in the cathode material without doping [122].

Many studies have shown that aluminum suppresses cation disorder. For example, the discharge capacities of LiNi<sub>0.47</sub>Al<sub>0.03</sub>Mn<sub>0.5</sub>O<sub>2</sub> and LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathode materials have capacity retention values of 78.5 and 68.8% after 150 cycles at 25 °C and 0.2 C cycle rate, respectively. These values are 70.8% and 69% at 60 °C [123]. This can be explained by the fact that aluminum doping reduces the Li/Ni mixture on LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and provides structural stability and subsequently improves the capacity and capacity retention [124]. Aluminum can also tune the H2-H3 phase transformation to reduce mechanical degradation. However, more than 5-6 mol% leads to secondary phase formation in the structure [125]. Recently, studies on cobalt-free NMA as a replacement for NCM and NCA cathode have been ongoing. Based on a study, the amount of RLC in NMC-89, NCA-89, NMCAM-89 and NMA-89 cathode materials are 2583, 2856, 2748 and 2532 ppm, respectively. NMA-89 has less amount of RLC. The Li/Ni mixture is 3% in NMA-89 and 3.3% in NMC-89. After 1000 cycles in the range of 2.5-4.2 V and at a cycle rate of 0.5C-1C at 25 °C, NMA-89 achieved 82% capacity conservation, outperforming NMC with 54% capacity conservation and NCA with 62% capacity conservation. The cycling performance is comparable to commercial NMC-622, but NMA-89 achieved 175 mAhg<sup>-1</sup> at first discharge capacitance, 15 mAhg<sup>-1</sup> more than NMC-622 [125].

### **Surface coating**

The surface coating can prevent any possible reconnection between the electrode and the electrolyte. In this way, oxygene loss from the structure can be prevented. Sun et

al. coated  $\text{AlF}_3$  on  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  at high current and obtained a capacity value of  $50 \text{ mAhg}^{-1}$  in the pristine structure and  $130 \text{ mAhg}^{-1}$  in the surface coated cathode material [126].  $\text{AlF}_3$  prevented the corrosion of the nickel-rich oxide structure by HF by providing the formation of oxygen vacancies and reducing the impedance [127]. The same cathode material was also coated with 3%  $\text{Li}_2\text{SiO}_3$  and the discharge capacity was improved by 20% over the uncoated cathode material. When coated with  $x\text{Li}_4\text{SiO}_4-(1-x)\text{Li}_3\text{PO}_4$ , a 13% discharge capacity increase was observed at 7C [128]. Even when tested at  $60^\circ\text{C}$ , 3 mol%  $\text{Li}_2\text{SiO}_3$  coating helps in maintaining the capacity by increasing the lithium ion diffusion rate by 1.6 times [129].  $\text{Li}_2\text{ZrO}_3$  coating together with  $\text{Zr}^{4+}$  doping provides many advantages such as maintaining cell voltage, stopping polarization, preventing cation exchange and reducing resistance. After 120 cycles, 97% capacity retention is achieved when the coating is as low as 1 mol%, while 3 mol%  $\text{Zr}^{4+}$  doped  $\text{Li}_2\text{ZrO}_3$  coating provides almost 100% capacity retention [130]. The addition of  $\text{Al}_2\text{O}_3$  into the electrolyte provides in situ modification of the nickel-rich structure. Physical protection is also possible by preventing corrosion and metal ion dissolution. As a result, the capacity at the end of 300 cycles at  $55^\circ\text{C}$  is  $129 \text{ mAhg}^{-1}$  [129], [130]. Core-shell structures also stand out as an alternative method in these developments. For example, in  $\text{Li}[(\text{Ni}_{0.9}\text{Mn}_{0.1}\text{O}_2)_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x]\text{O}_2$  core-shell structure,  $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$  core provides high capacity while  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  shell provides thermal and structural stability. After 50 cycles, the capacity retention of the shell structure is 87.7%, while the core structure has 76.9% capacity retention [131]. These concentration gradient structures can be tuned according to particle size, shell thickness, heat temperature, time and lithiation time. However, this tuning is very difficult due to intermediate diffusions in the core and shell regions.

Conductive polymers can also be used in the coating. For example, the  $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$  cathode with PEDOT:PSS shows a capacity value of  $128.03 \text{ mAhg}^{-1}$  and 87.1% capacity retention up to 30 cycles at 0.1C. Most importantly, grain boundary engineering (GBE) can also suppress particle breakage [132]. Cheng et al. combined surface coating and GBE by coating  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  cathode with  $\text{Li}_3\text{PO}_4$  by atomic layer deposition. With these two techniques, 91% capacity retention was achieved after 200 cycles in the 2.7V-4.7V range [133].

## **Elektrolyte Additives**

Nickel is sensitive to excessive reduction during charging. This can cause the electrode to react with the electrolyte and produce insulating by-products [104], [134]. Additives to conventional carbonate-based electrolyte produce uniform and strong CEI. This helps to suppress phase transformation, prevent microcrack formation, stop HF formation and prevent TM dissolution. For example,  $\text{LiPF}_6$ -based electrolytes are highly prone to decompose and form HF,  $\text{POF}_3$  and  $\text{PF}_5$ . The TMS group removes residual lithium and the resulting compound decomposes  $\text{PF}_5$  [135]. Additives can not only remove harmful components but also provide an in-situ layer during cycling, creating a long-lasting electrode material [136].

## **Single Crystal Technology**

Single crystal technology does not allow the development of materials with high uniformity and high density. Single-grain crystalline materials have stronger particles and more stable structures than polycrystalline materials. This strength is extremely important in rolling processes [137]. When polycrystalline NMC is compared with single crystalline NMC, it is seen that the anisotropic volume change of single crystalline NMC is less and the crack formation in it is minimized [138]. Therefore, this less crack formation means that the frequency of side reactions between the electrode and the electrolyte is reduced [139]. In polycrystalline materials, severe side reactions between the electrode and the electrolyte can occur, resulting in structural degradation, enabling the transition from a non-reversible layered structure to a rock-salt phase structure. The disordered or salt structure hinders the diffusion of lithium ions and leads to capacity depletion. Moreover, the monocrystalline structure prevents the formation of anisotropic stress during the charge cycle. Xu et al. synthesized particles along the (010) plane and reduced the resistance to lithium ion diffusion across the electrode. In addition, the volume change decreased drastically and prevented possible pulverization [140]. Bi et al. synthesized a micro-scale single grain crystal structure, and microcracks were observed when the single crystal material was charged and the lithium ion was completely removed from the system. However, when the material was discharged again, most of the signs of microcracks disappeared [141]. An important point is that the addition of a small amount of  $\text{LiPF}_6$  to the sludge during the electrode coating stage allows the removal of RLCs on the surface without

affecting the process. In this way, the unwanted RLCs are converted into  $\text{Li}_3\text{PO}_4$  and  $\text{LiF}$  and these components are well suited for a stable SEI.

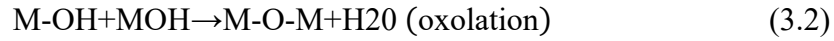


### 3. SYNTHESIS TECHNIQUES

#### 3.1 Sol-gel

The sol-gel process is a chemical synthesis method in which precursors are polymerized by hydrolysis and condensation reactions. Unlike solid-state synthesis methods, sol-gel synthesis can be controlled at the molecular level. In this way, synthesis with high purity, homogeneity and uniform crystal structure can be realized. In the sol-gel process, it can be difficult to control the process due to the solvent function of water, its ability to form ligands and the reactivity of precursors to water. In addition to these, many parameters such as pH, temperature, mixing mode, oxidation, hydrolysis and condensation rate are highly effective in the reaction process. Precursors used in the sol-gel process can be metal alkoxides or metal salts. Metal alkoxides can be expressed as  $M(OR)_n$  and metal salts as  $M_mX_n$ . Since the solubility of metal alkoxides in water is low, they are usually dissolved in alcohol and the OR group in metal alkoxides is very sensitive to moisture, heat and light. For metal salts, pure water can be used as solvent. The reaction can be slowed down by introducing less water than the required amount and this amount of water is evaluated based on the water/alkoxy ratio [142]. The sol-gel process can take place with or without a catalyst [143]. The basic steps of a sol-gel process consist of hydrolysis of the precursor, condensation of active species, gelation, aging, drying and high temperature treatment. Sol can be defined as a suspension of colloidal solid particles in a liquid [144]. Practically, these solid particles range in size from 2 nm to 0.2  $\mu\text{m}$ . Peptization, which occurs during hydrolysis and condensation reactions, is a decoagulation event that can be defined as the dispersion of precipitates with the help of a solvent. Coagulation is the growth and precipitation of colloidal grains as a result of zero electric charge. The progression of hydrolysis is shown in equation (3.1), (3.2) and (3.3). Sol structure is formed as a result of peptization. Hydrolysis and condensation reactions reduce the viscosity of the sol until a gel structure is formed. Condensation reactions then occur on the sol [145]. The gelation process starts with the agglomeration of polymers or particles in fragmented clusters, after which the clusters interpenetrate each other to

some extent. Eventually they bind together to form the final network structure [144]. When the extent of polymerization and cross-linking of polymeric molecules increases, the entire solution solidifies and the cross-structure is formed. As the chain length or number of coordination increases, it becomes more difficult to break the O-R bond and the hydrolysis rate decreases, while increasing the number of coordination also increases the chemical reactivity [145].



The stage following the formation of the gel from the sol structure by hydrolysis and condensation reactions is the aging stage. The period expected for a wet gel to be stored for a long time and transformed into a stable structure by the reactions carried out by the chemicals in it is called the aging process. Depending on the method of performing the drying stage, which is critical in the sol-gel process, the gel is basically produced as 3 different intermediate products as aerogel, xerogel and criogel. Aerogels obtained by supercritical drying are generally low density and monolithic materials [146]. Xerogels are obtained by drying at approximately ambient temperature and at atmospheric pressures. Drying methods can be varied and sintering can be performed after drying as required by the process. A schematic representation of the products resulting from different Sol-gel processes is given in Figure 3.1. In summary, the advantages of the sol-gel process are that it can be carried out at room temperature, high purity products can be obtained, homogeneous doping, mild chemical conditions and controllability of requirements such as pores and dimensions in the product structure. The disadvantages are that precursor materials are expensive, the process is time-consuming, and it is very difficult to achieve long and continuous production and industrialization [147].

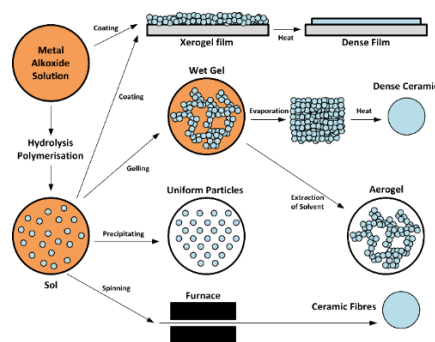


**Figure 3.1:** Different sol-gel processes [145].

### 3.2 Solid-state

In solid-state calcination, the final cathodes are often produced without the preparation of precursors using the all-solid-state approach. This approach is straightforward and very easy to scale up. However, the components in the raw materials can scarcely be combined homogeneously at the atomic level due to the peculiarities of powder mixing. Additionally, because of their variable particle shape and particle sizes varying from submicrometers to a few micrometers, the products produced by the all-solid-state approach have lower tap densities [148].

A significant benefit is the simplicity with which transition metal (TM) and Li stoichiometry may be achieved by careful monitoring of the constituent powders - albeit, depending on the processing and particle size, extensive hold durations at extreme temperatures may be required [149–151]. In solid-state synthesis, a very high temperature and a lengthy firing time are often required. High pressure, vigorous milling, and pellet production have occasionally been used in addition to the prolonged fire periods at high temperatures, which have significant energy requirements, to ensure high phase purity [44], [152], [153]. Due to the requirement for TM (transition metal) and Li (lithium) elements to traverse significant distances within solid phases during solid-state synthesis, the diffusion process can be expedited through the application of elevated temperatures and ensuring intimate contact between constituents. Extended firing times facilitate the attainment of equilibrium in the solid structure. Another issue arises from variations in preparation conditions, such as firing temperature and cooling rates, which can impact the extent of oxygen loss or absorption in the resulting materials. This, in turn, can affect the phase purity of the final products [154], [155]. Extended periods of high-temperature firing can result in the loss of lithium (Li) from the material, leading to potential impacts on the electrochemical and/or phase behavior of the active material [156], [157]. Aggressive firing conditions present the challenge of material metastability, wherein changes in oxidation states of different elements and even phase transitions can occur due to oxygen loss and the influence of high temperatures, particularly in transition metal (TM) oxides containing nickel [158], [159]. An alternative approach is to subject the materials to relatively lower temperatures (400–600 °C) for extended durations, potentially spanning several days. However, even with this method, significant time

and energy resources are still required [151]. A schematic representation of a solid-state synthesis is shown in Figure 3.2.

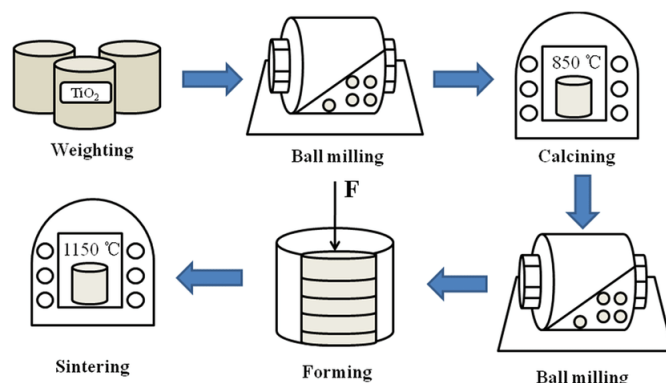


**Figure 3.2:** A schematic representation of a solid-state synthesis [160].

### 3.3 Solution Combustion

Combustion synthesis enables the production of a diverse range of cathodes and anodes with varying structures for rechargeable lithium-ion battery (LIB) applications. By adjusting fundamental factors such as the choice of fuel-oxidant combination and the ratio of fuel to oxidizer, the electrode's stoichiometry and morphology can be precisely tailored. Specifically, this combustion process conducted at relatively low temperatures results in electrode materials with large surface areas and well-defined porous structures, which promote improved wetting of the electrolyte, enhanced ion movement, and superior lithium storage capabilities. Moreover, this synthesis method is rapid, straightforward, and efficient in terms of energy and time consumption. It offers the advantage of identifying potential metastable electrodes with unique electrochemical properties that can be easily scaled up for large-scale production.

comparison to alternative solution-based methods, combustion synthesis offers several advantages. Firstly, it enables the rapid synthesis of highly substituted oxides in a single step. Additionally, it provides a unique advantage of quasi-atomic dispersion or atomic level mixing of the constituent cations within the liquid precursors. This characteristic facilitates the synthesis of crystallized powders characterized by small particle sizes and high purity, all achieved at low temperatures [161]. The quantity of fuel used has a significant impact on the morphology of the synthesized product. Inadequate fuel can prevent some transition metals from oxidizing during burning in an inert atmosphere and prevent the creation of the intended crystal structure, as observed in the case of spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [162].

The reaction occurred within a timeframe of less than 5 minutes and involved boiling, ignition, and decomposition of the solution. This decomposition process generated substantial amounts of gases, specifically nitrogen and ammonia oxides. Notably, it is important to highlight that oxygen present in the air does not actively participate in the combustion reaction. Instead, oxygen derived from the oxidizer in the precursor solution is utilized. While the precise chemical mechanisms underlying solution combustion synthesis are challenging to pinpoint, it can be reasonably assumed that thermal decomposition, as well as the formation or combustion of metal complexes or gases, occur during the decomposition process. The exothermic reaction during combustion synthesis generates extremely high levels of energy, often surpassing a flame temperature of 1000 °C. This intense energy is more than adequate for the direct formation of the desired final product, which predominantly comprises oxides [162].

The outcome of solution combustion synthesis (SCS) is primarily determined by the composition of three main constituents: oxidizer, fuel, and solvent. The oxidizer is typically selected from various metal salts, such as nitrates, carbonates, and sulfates. The fuel consists of reducing agents, including hydrocarbons like urea and different hydrazides. Water is commonly used as the solvent in SCS. Hydrated nitrates are particularly suitable oxidizers due to their lower decomposition temperature, cost-effectiveness, and easy availability. Moreover, nitrates have higher solubility in ambient water compared to sulfates or carbonates. Among available fuels, urea is preferred due to its affordability, ready availability, water solubility, neutral ligand properties, and ability to form stable complexes with metal cations, particularly nitrate-based ions. Urea is also highly reactive due to the presence of two active amino groups [163]. Metal-urea complexes are low-cost, environmentally less toxic, easily handled, and serve as effective precursors for material synthesis [162].

The fuel has two functions: it creates complexes with metal ions to facilitate uniform mixing of the cations in the solution, and it burns to release heat in an exothermic process by producing CO<sub>2</sub> and H<sub>2</sub>O. There is no need for an external source of heat because the chemical reaction produces all of the heat needed for it. To acquire the precursor for combustion, two distinct techniques are used. As is frequently seen in the solution combustion process, the first technique uses a reactive solution in a vessel kept at 250–300 °C to initiate combustion and ultimate product synthesis in a single phase. The second technique, called gel combustion synthesis, is letting the first

solution dry until the solvent's boiling point is reached, at which time the solution gels. [164], [165]. Figure 3.3 illustrates a schematic example of solution combustion synthesis.

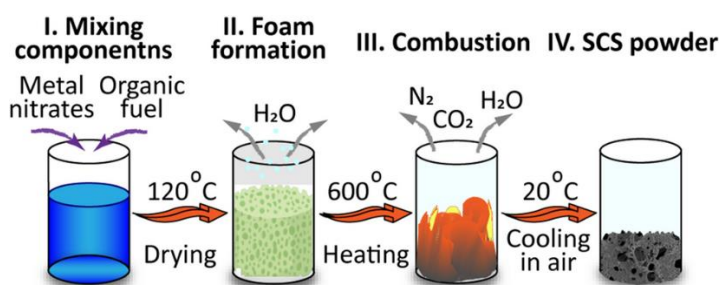


**Figure 3.3:** A schematic view of solution combustion process [166].

### 3.4 Hydrothermal

Hydrothermal synthesis is based on obtaining crystal products by adding raw liquid materials into a system called an autoclave operating at high pressure and temperature. The process is shown schematically in Figure 3.4. As the materials interact with the cooler zone of the autoclave, crystalline products are formed [167]. Although the solid state and combustion synthesis is quite simple, the cathode active particles are not homogeneously dispersed and agglomeration occurs. In hydrothermal synthesis, cathode materials with better particle distribution, high purity and low production cost can be obtained. In this way, the produced cathode materials have better electrochemical properties [168]. In the hydrothermal synthesis method, it takes place at low energy without creating waste material. It is quite similar to the solvothermal synthesis method. The difference between them is that the precursor materials contain water in hydrothermal synthesis [169]. Water can dissolve even non-ionic compounds at high pressure and temperature. In this method, particle morphology and structure can be controlled by changing the precursors and conditions [170]. Since it is a reproducible method with better nucleation, it is a highly preferred synthesis method for nanostructures [169]. However, the biggest disadvantage is the difficulties in controlling the size and shape of the final product. The reason for this is that many parameters such as production type, concentration volume, properties of precursors, mixing, time, pressure and drying temperatures play an important role during the synthesis [171]. In addition, a costly autoclave requirement, high quality seed

requirement, high temperature and difficulty in monitoring during nucleation are other factors that make this synthesis challenging [169].

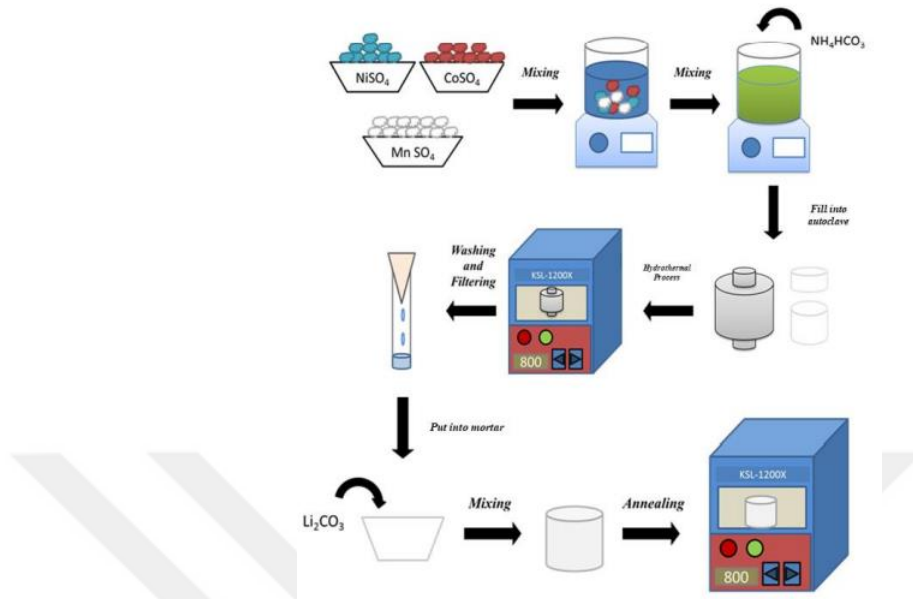


**Figure 3.4:** Schematically NMC811 production by hydrothermal synthesis [172].

Hydrothermal synthesis method is an important method used in the production of cathode materials and is very suitable for a wide range of olivine materials. These may contain a single metal ion and its mixture. The alignment of lithium and metal ions occurs above about  $175^\circ\text{C}$ . A product with a good crystalline structure and a particle size of microns, which can be reduced to 20 nm, and a thickness of several hundred nanometers can be obtained [173]. As the diffusion path of lithium ions is shortened and electron transport in the synthesized structure increases, the cathode material performs better. Addition of ethanol or glycol in the hydrothermal synthesis method may further reduce the particle size [174]. This synthesis method is one of the most popular methods used especially during the synthesis of LFP-based cathode materials [171].

### 3.5 Spray Pyrolysis

The spray pyrolysis (SP) method is widely used for the production of fine-grained powders due to its economic and versatile nature compared to gas condensation methods like plasma reactors and laser ablation, as well as techniques like sol-gel. The SP method allows for the production of micro-nano particles with a wide range of chemical composition and morphology, which are spherical and unagglomerated. It

enables the preparation of metallic and intermetallic compounds, as well as ceramic materials, in the form of powders and thin films [175]–[177]. In a conventional SP method, a water-based solution containing the material to be produced is atomized, resulting in the formation of an aerosol consisting of initial droplets. The aerosol is then transported into the furnace environment using a carrier gas, where solid particle formation occurs through a solid-state reaction [177]. The general principle of the SP method involves the formation of an aerosol from the solution containing the material to be produced, followed by thermal decomposition reactions that lead to the desired composition of the particles. The SP method typically consists of four steps: formation of aerosol droplets from the solution, evaporation and drying of the droplets, transformation (reaction) of the droplets, and solid particle formation [175]–[179]. The spray pyrolysis method can be performed using different types of atomizers, and various spray pyrolysis techniques are illustrated in Figure 3.5.

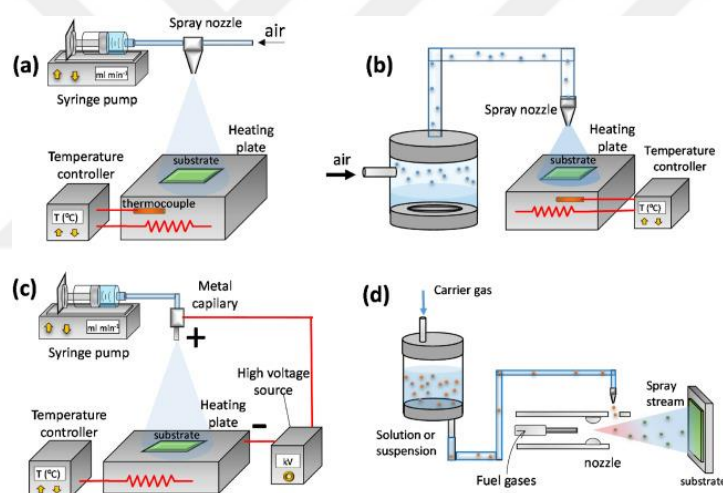


**Figure 3.5:** The diagram illustrates various spray-pyrolysis techniques: (a) CSP. (b) USP. (c) ESP. (d) FSP [180].

This technique has always been appealing because it involves a simple and inexpensive process compared to other materials, making it suitable for large-scale production. However, the particles obtained from the spray pyrolysis process are not stable when exposed to high temperatures during sintering. This instability leads to the breakage of spherical particles in the cathode material. Additionally, the decomposition of nitrate content produces nitrous oxide, which is considered a harmful greenhouse gas. Furthermore, the particles have a relatively small average size ( $<4\ \mu\text{m}$ ), which can negatively impact the electrochemical performance, particularly the cycling ability.

This is due to the increased reactivity caused by the large surface area of the small particles interacting with the electrolyte during the charge/discharge process [181].

### 3.6 Co-precipitation

Co-precipitation is one of the most widely used methods for the synthesis of layered oxide structures. It allows for homogeneous mixing of the elements, the production of dense particles with a narrow size range and is suitable for continuous production. A typical co-precipitation process consists of precipitation of precursor materials in a reactor, filtration, drying and calcination of the resulting precipitate. A schematic description of these steps is shown in Figure 3.6. This method is usually carried out by precipitating the products in the form of hydroxides or carbonates. After precipitation, the structure in the form of hydroxide or carbonate is transformed into an oxidised structure by changing the anionic groups after calcination. The mass fraction of anionic groups in carbonate structures is higher, the gas output ( $\text{CO}_2$ ) is higher and a less dense structure is obtained, making hydroxide precipitation advantageous [182].

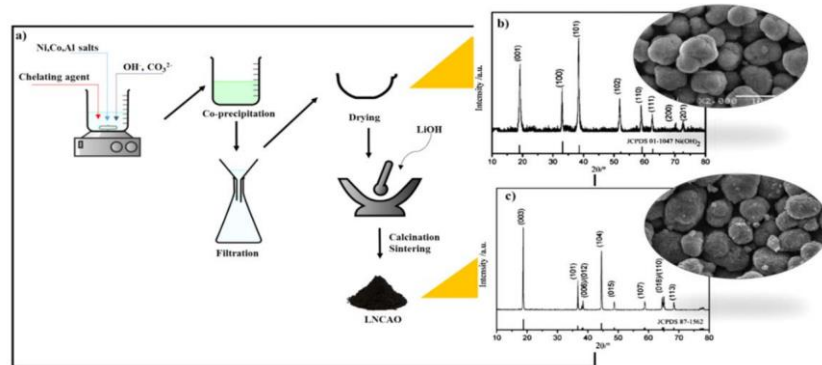


**Figure 3.6:** a) Schematic visualization NCA via co-precipitation b) XRD and SEM analyses of the NCA [182].

Precursor materials are usually sulphate or nitrate based. Sulphate-based salts are preferred because they are more economically advantageous. Apart from the precursor material, a precipitating or chelating agent is also used during a co-precipitation synthesis.  $\text{NaOH}$  as precipitant and  $\text{NH}_4\text{OH}$  as chelating agent are the most commonly used solutions. Precursor materials, precipitating and chelating agents are very important aspects that strongly influence the electrochemical performance, since the composition, particle size, crystalline and structural order and the amount of impurity are closely related to these materials. The first parameters that come to mind and affect

the co-precipitation method can be listed as reactants, pH, temperature, feed rate, stirring speed, reactor type and mixer type. These parameters are indicated in Figure 3.7 [148].

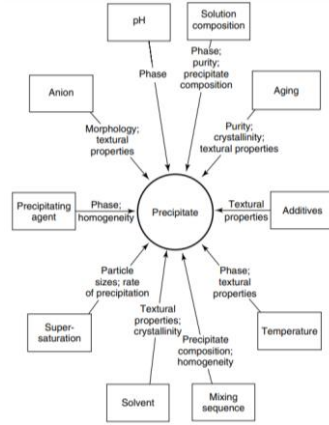
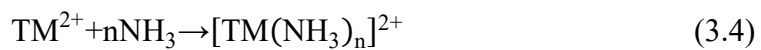


**Figure 3.7:** The parameters affecting co-precipitation process [183].

The structures obtained in the synthesis of nickel-rich materials are usually spherical with a diameter ranging from a few micrometres to 10 micrometres. Typically, the co-precipitation process proceeds through the mechanisms in Equation 3.4 and Equation 3.5. As can be seen from the equations, there is a competitive relationship between complexation and precipitation which leads to precipitation and recrystallisation and makes it a controllable process. Based on this mechanism, the growth of hydroxide precursors takes place in 3 steps as shown in Figure 3.8. First, nucleation occurs when solutions initiate supersaturation. The growth can be controlled by pH and chelating agents and the nuclei grow into single crystalline grains. Secondly, these single crystals agglomerate together to form polycrystalline and precursor particles. Thirdly, spherical secondary particles are formed by embryonic agglomeration, growth of primary particles and adhesion of primary particles, which grow and agglomerate to become spherical. In Equation 3.6, the consolidation and smoothing of the surface due to the repulsive force of surface free association is indicated by the Kelvin equation [148].



$$\ln\left(\frac{S}{S_0}\right) = \left(\frac{2\sigma}{p_1}\right)\left(\frac{M}{\rho RT}\right) \quad (3.6)$$

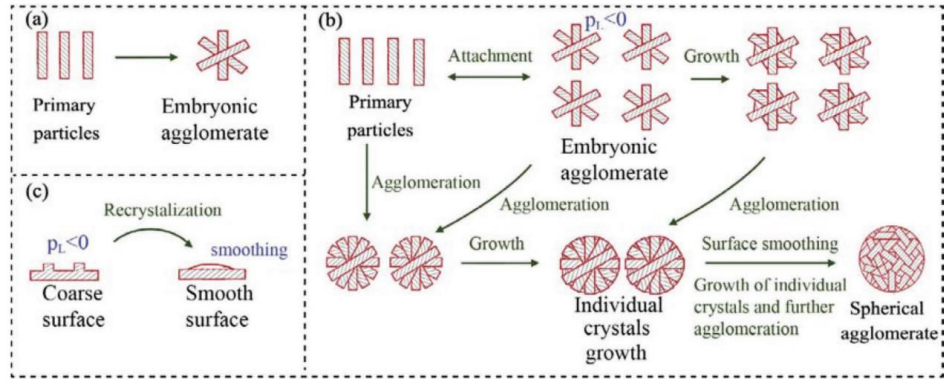


**Figure 3.8:** Illustration of a) embryonic agglomerate b) secondary particle c) recrystallization mechanism [148].

$M$  is the molecular mass of the crystals,  $\rho$  is the crystal density,  $R$  is constant,  $T$  is the temperature, and  $S$  and  $S_0$  are the solubility of the crystals on the curved surface.  $\sigma$  is the solid and liquid surface tension.  $S$  is smaller than  $S_0$  and  $p_L$  is negative if the crystal surface is concave. This demonstrates that surfaces that are concave are more suited for recrystallization. The secondary particles formed by this mechanism are denser and smoother. A dynamic equilibrium between precipitation and dissolution leads to the development of dense spherical particles, which is extremely sensitive to supersaturation. Apart from density and sphericity, issues such as alignment and orientation are also very important. This is because the diffusion of lithium ion and the mechanical stress during charge-discharge are closely related to these issues.

Co-precipitation is the phenomenon in which normally soluble components are precipitated simultaneously with a macro-component from the same solution, i.e. the parent solution. Knowledge of the co-precipitation mechanism is useful in designing the co-precipitation procedure. The phenomenon of co-precipitation is quite complex and can generally be attributed to the following mechanisms such as surface adsorption, occlusion, inclusion, mixed crystal formation and subsequent precipitation, shown in Figure 3.9 [148], [183].

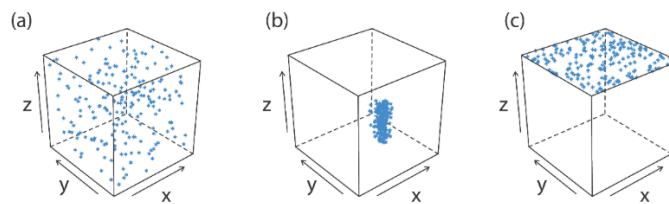


**Figure 3.9:** Schematic illustration of a) inclusions, b) occlusions, and c) surface adsorbates [184].

The comparison of the co-precipitation method with other methods is shown below in Table 3.1. In addition to having controllable purity and particle size, it can be industrialised and is advantageous in terms of ease of equipment, which makes it advantageous compared to other synthesis methods.

**Table 3.1:** Comparison of methods to produce cathode materials in terms of their advantages and disadvantages [185].

|                             | SOLID-<br>STATE | CO-<br>PRECIPI<br>TATION | SOL-GEL   | MICROWAVE | HYDRO<br>THERMAL | SPRAY<br>PYROLYSIS |
|-----------------------------|-----------------|--------------------------|-----------|-----------|------------------|--------------------|
| <b>Purity</b>               | Low             | Moderate                 | High      | Moderate  | High             | High               |
| <b>Particle size</b>        | Big             | Medium                   | Small     | Small     | Big              | Small              |
| <b>Agglomeration</b>        | Yes             | Yes                      | No        | Yes       | No               | No                 |
| <b>Equipment complexity</b> | Simple          | Simple                   | Simple    | Simple    | Complex          | Complex            |
| <b>Reactive period</b>      | Long            | Moderate                 | Moderate  | Short     | Long             | Short              |
| <b>Energy consumption</b>   | High            | Moderate                 | Moderate  | Low       | High             | Moderate           |
| <b>Reaction control</b>     | Easy            | Difficult                | Easy      | Difficult | Easy             | Moderate           |
| <b>Industrialisation</b>    | Moderate        | Easy                     | Difficult | Difficult | Difficult        | Easy               |
| <b>Performance</b>          | Low             | Moderate                 | Good      | Moderate  | Moderate         | Good               |

#### 4. EXPERIMENTAL STUDIES

In the studies and experiments carried out, it was aimed to synthesise the cathode materials shown in Table 4.1 with the specified compositions.

**Table 4.1:** Synthesised cathode materials with their compositions.

| Cathode Material                                                             | Abbreviation |
|------------------------------------------------------------------------------|--------------|
| $\text{LiNi}_{0.6}\text{Fe}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.1}\text{O}_2$   | NFAM-6211    |
| $\text{LiNi}_{0.8}\text{Fe}_{0.1}\text{Al}_{0.05}\text{Mn}_{0.05}\text{O}_2$ | NFAM-8155    |

The synthesis of the cathode materials indicated in Table 4.1 was achieved by co-precipitation method. Lithium Hydroxide Monohydrate (TEKKIM,  $\text{LiOH}\cdot\text{H}_2\text{O}$ ), Nickel(II) sulfate hexahydrate (MERCK,  $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ ), Iron(II) Sulfate Heptahydrate (ISOLAB,  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ), Aluminium sulfate hydrate (MERCK,  $\text{Al}_2(\text{SO}_4)_3\cdot \text{H}_2\text{O}$ ) and Manganese(II) Sulfate Monohydrate ( $\text{MnSO}_4\cdot \text{H}_2\text{O}$ ) were used. Sodium hydroxide (ISOLAB,  $\text{NaOH}$ ) was used as precipitant and ammonium hydroxide (MERCK,  $\text{NH}_4\text{OH}$ ) was used as chelating agent.

For each experiment, firstly, 60mL, 2M transition metal solution for each cathode material was prepared with distilled water and the solution was stirred in a magnetic stirrer for a certain time and then made ready for feeding. Then, 60 mL, 4M sodium hydroxide solution with saff water as a precipitating agent and 60 mL, 2M ammonium hydroxide solution as a chelating agent were prepared for each experiment.

At the beginning of each synthesis, 300 mL of pure water was poured into the glass reactor and the reactor was closed with an airtight lid. The pure water in the reactor system was first heated to 50°C by means of a hot plate and the pH was adjusted to 11.5 which is within the operating range. During this time, nitrogen was fed to the reactor and the system was swept with gas. Then, transition metals solution, sodium hydroxide solution and ammonium hydroxide solution were fed into the reactor with nitrogen gas by pneumatic flow controller. The feed rates of the transition metals were calculated as 0.3-0.4 mL/minute on average throughout the experiments and the pH of the system was kept in the range of 11.30-11.55 during each experiment and the

precipitating agent was added to the system to maintain this pH range. The synthesis was carried out under nitrogen atmosphere throughout. In this way, oxidation of transition metals was prevented. At the same time, the system was continuously stirred with a mechanical stirrer at 500 rpm at 50°C. The experimental setup and system are shown in detail in Figure 4.1.

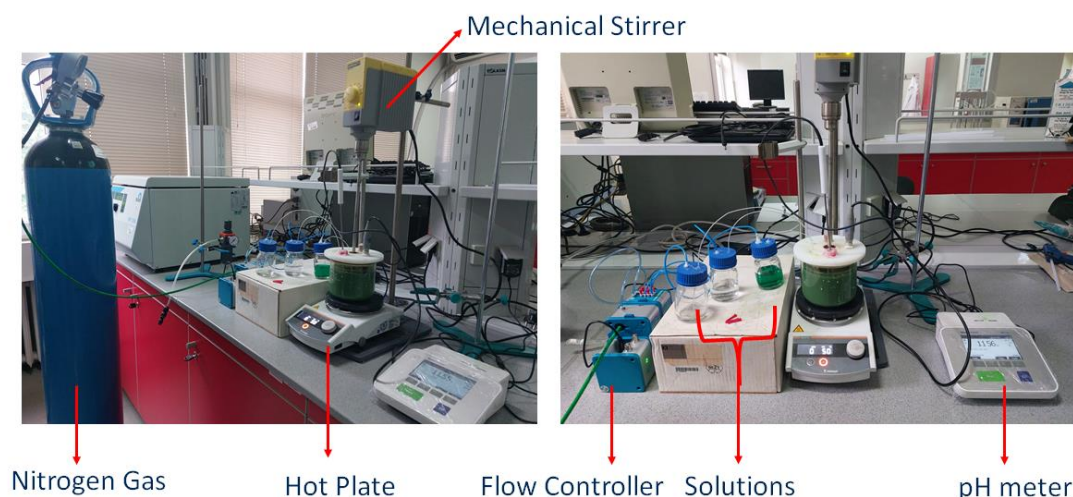


**Figure 4.1:** Experimental setup for co-precipitation process.

Centrifugation and filter paper methods were used to filter and wash the resulting hydroxide solution. Washing was continued until neutralised and approximately 3L of distilled water was used for each wash. The neutralised solid samples were then placed in a vacuum oven overnight for drying. At the end of the day, the dried samples were ground in a ball-mill for mixing with lithium hydroxide. Lithium hydroxide was added so that the mole ratio of lithium was 1.05 to the mole ratio of the samples in hydroxide form. Then, the powders in the form of hydroxide with added lithium source were first heat treated at 500°C for 6 hours to remove some organics from the structure and then at 750°C for 12 hours for calcination. Calcination was carried out both atmospherically in the muffle furnace and in the tube furnace by blowing oxygen into the system (1 bar). The final powders obtained after calcination were ground and prepared as active material.

The obtained powder samples were mixed with an appropriate amount of 6% PVDF binder dissolved in NMP to obtain a slurry for coating. The slurry was then prepared as 80 % active material, 10 % carbon black and 10 % PVDF by weight. Before coating, the surface to be coated was sanded with sandpaper and the slurry was applied to the

foil surface with a thickness of approximately 300 micrometres. Then the sample coated on the foil surface was left to dry in an oven.

After the drying process was completed, the cathode discs were punched with a 13mm diameter puncher. Then the coin cell assembling stage was started. Coin cells were made in a glovebox (MBRAUN) operating under argon atmosphere with H<sub>2</sub>O and O<sub>2</sub> less than 1 ppm. The coin cell was assembled from the lower case to the upper case with the cathode electrode with the coated surface facing upwards, appropriate amount of electrolyte, separator, appropriate amount of electrolyte, lithium metal, spacer and finally spring. The obtained 2032 coin cell batteries were removed from the glovebox for galvanastatic charge-discharge. The flow chart showing the whole process is shown in Figure 4.2.



**Figure 4.2:** Flowchart of all process.



## 5. RESULTS AND DISCUSSION

### 5.1 X-ray Fluorescence (XRF) Analysis

X-ray fluorescence (XRF) analysis of NFAM-6211 and NFAM-8155 samples was performed with BrukerS8 Tiger. XRF results are given in Table 5.1. Based on Table 5.1, it can be said that silicon and sulphur containing impurities are observed in the produced samples. The source of these impurities is thought to be the glass reactor in which the co-precipitation process takes place and the sulphate-based metal salts used in the experimental process, respectively.

**Table 5.1:** XRF result of NFAM-6211 and NFAM-8155.

| %<br>Sample | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | K <sub>2</sub> O | CaO  | MnO  | Fe <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | SO <sub>3</sub> | Cl    | NiO   | LOI  |
|-------------|-------------------|--------------------------------|------------------|------------------|------|------|--------------------------------|--------------------------------|-----------------|-------|-------|------|
| NFAM-6211   | <0,01             | 4,73                           | 0,40             | <0,01            | 0,03 | 8,30 | 19,61                          | <0,01                          | 5,02            | <0,01 | 55,02 | 6,89 |
| NFAM-8155   | <0,01             | 1,85                           | 0,41             | 0,01             | 0,02 | 4,20 | 10,10                          | <0,01                          | 1,09            | <0,01 | 74,54 | 7,68 |

When the atomic mole fractions for NFAM-6211 and NFAM 8155 samples are calculated from the XRF results, the data in Table 5.2 are encountered. Therefore, it is seen that the chemical names of the samples intended to be produced as NFAM-6211 and NFAM-8155 are  $\text{LiNi}_{0.62}\text{Fe}_{0.21}\text{Al}_{0.08}\text{Mn}_{0.1}\text{O}_2$  and  $\text{LiNi}_{0.82}\text{Fe}_{0.1}\text{Al}_{0.03}\text{Mn}_{0.05}\text{O}_2$ , respectively.

**Table 5.2:** Atom mol fractions of NFAM-6211 and NFAM-8155.

| Material  | Atom mol fractions |      |      |      |
|-----------|--------------------|------|------|------|
|           | Ni                 | Fe   | Al   | Mn   |
| NFAM-6211 | 0,62               | 0,21 | 0,08 | 0,10 |
| NFAM-8155 | 0,82               | 0,10 | 0,03 | 0,05 |

In addition, during the synthesis process, the washing method was optimised based on the XRF results and a change was made from centrifugal washing to filter paper filtration. When Table 5.3 is compared with Table 5.1, the impurities analysed in the centrifugally washed samples, different from the filter paper filtration method, can be clearly seen. Therefore, it has been demonstrated that centrifugal washing is not suitable for washing large samples in terms of mass and volume.

**Table 5.3:** Impurities when solution is washed by centrifuge.

|           | %    | Na <sub>2</sub> O | K <sub>2</sub> O | CaO |
|-----------|------|-------------------|------------------|-----|
| Material  |      |                   |                  |     |
| NFAM-6211 | 0.65 | 0.13              | 0.12             |     |
| NFAM-8155 | 0.80 | 0.14              | 0.11             |     |

## 5.2 X-ray Diffractometer (XRD) Analysis

Firstly, calcination and oxidation of NFAM-6211 and NFAM-8155 samples were carried out in an atmospheric furnace. However, when the I(003)/I(104) ratio in Figure 5.1 is analysed, it is seen that there is a lot of lithium and transition metal mixture in the system. The reason for this is the oxygen vacancies and reduction of  $\text{Ni}^{3+}$  [186]. The reason for this situation is explained in more detail in the following sections. In Figure 5.1, the ratio of I(003)/I(104) is 0.7 and no splitting is observed in the (006)/(012) and (018)/(110) peaks, indicating that the layered structure cannot be obtained. Therefore, in order to prevent this, the subsequent heat treatments were carried out in tube furnaces and oxygen was blown into the system at 1 bar level. When Figure 5.1 is compared with Figure 5.2 and Figure 5.4, it is clearly observed that this problem can be solved.

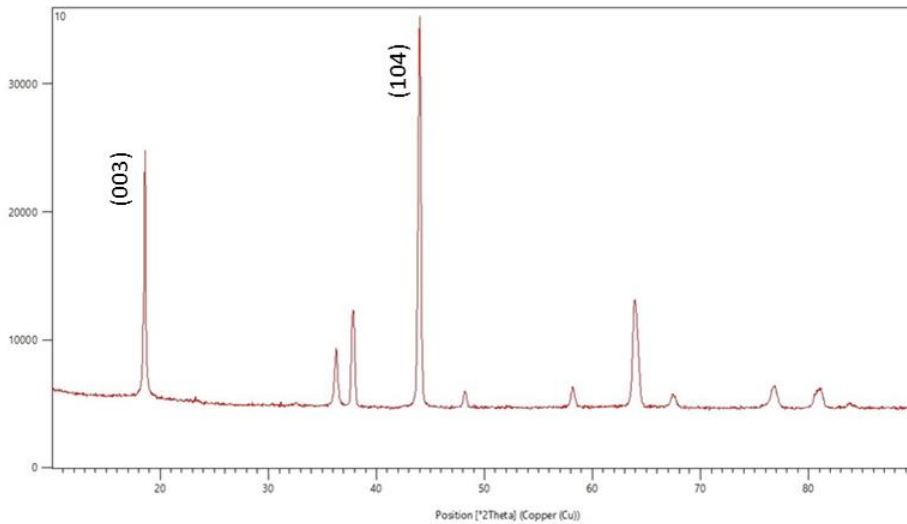


**Figure 5.1:** XRD results of after calcination of NFAM-8155 under atmospheric conditions without blowing oxygen.

Figure 5.2 shows the X-ray diffraction patterns (XRD) of the NFAM-6211 cathode material and the difference pattern data after Rietveld analysis. It is observed that the related cathode material has a single phase structure with the chemical name  $\text{Li}_{0.954}\text{Ni}_{0.0368}\text{Fe}_{0.0092}(\text{Ni}_{0.8}\text{Fe}_{0.2})\text{O}_2$  (COD ID: 1529126). The whole structure is  $\alpha\text{-NaFeO}_2$ -

type (space group R-3m). The very clear splitting seen in (006)/(012) and (018)/(110) peaks reveals that the obtained structure has high crystallinity, good hexagonal order and well-defined layered structure [187]. The intensity ratios of (003) and (104) indices, i.e.  $I(003)/I(104)$ , seen in XRD patterns give information about the Li/Ni mixture occurring in the structure and a ratio greater than 1.2 means that the Li/Ni mixture is at the desired level. The structural arrangement of the NCM is shown in detail in Figure 5.3, which includes the (003) and (104) lattice planes. The (003) plane with R-3m symmetry is filled with transition metal ions; On the other hand, the (104) plane with R-3m symmetry contains both lithium and transition metals. Therefore, the change of nickel in the 3b regions and lithium in the 3a regions in the structure significantly affects the  $I(003)/I(104)$  ratio [188]. The  $I(003)/I(104)$  ratio in Figure 5.2 was calculated as 1.18.

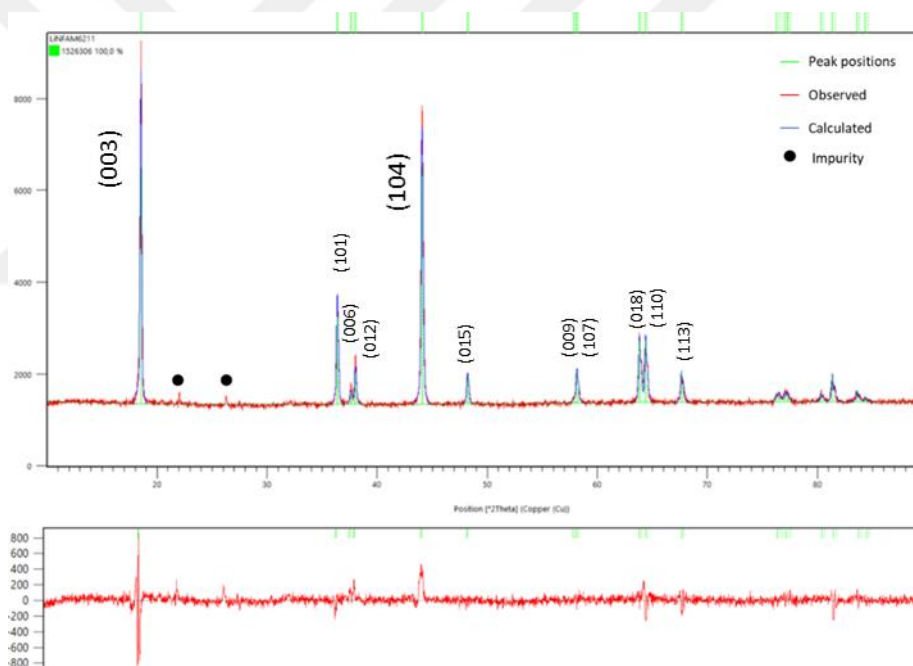


**Figure 5.2:** XRD analyses with difference pattern of NFAM-6211.

The reason for the difference in the difference pattern data on the (003) peak is the presence of impurities in the structure and marked on the XRD patterns. These impurities are thought to be sulfur based on XRF and EDS results. The fact that the observed peak is located further to the right than the calculated peak indicates that the lattice parameter of the structure is smaller. The fact that the ionic radius of the sulfur atom in the octohedral structure is 0.51 Å also supports this situation. Since the sulfur atoms in the structure prevented the formation of equal interplanar spacing and created

a structure with a more heterogeneous (003) interplanar distance, a deviation occurred in the difference pattern data.

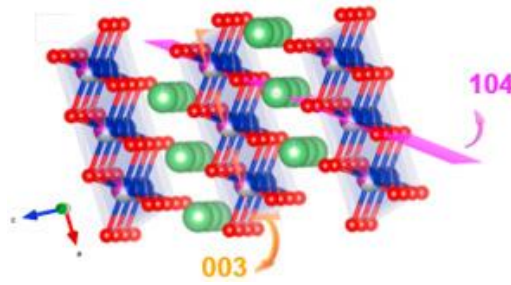


**Figure 5.3:** (003) and (104) planes in NCM cathode material [188].

Table 5.4 shows the structural parameters of NFAM-6211 cathode material by Rietveld analysis. Goodness of fit value of Rietveld analysis is 1.71. From Table 5.4, approximately 8.2% of all nickel atoms in the structure are replaced by lithium atoms, while approximately 2% of iron atoms are replaced by lithium atoms. The lattice parameters  $a$ ,  $b$ ,  $c$  and volume are 2.89024 Å, 2.89024 Å, 14.32804 Å and 103.654 Å<sup>3</sup>, respectively.

**Table 5.4:** Rietvel analysis and structural parameters of NFAM-6211.

| Element | x | y | z      | Occ.  | Site |
|---------|---|---|--------|-------|------|
| Li      | 0 | 0 | 0      | 0.946 | 3a   |
| Ni      | 0 | 0 | 0      | 0.05  | 3a   |
| Fe      | 0 | 0 | 0      | 0.004 | 3a   |
| Li      | 0 | 0 | 0.5    | 0.054 | 3b   |
| Ni      | 0 | 0 | 0.5    | 0.56  | 3b   |
| Fe      | 0 | 0 | 0.5    | 0.197 | 3b   |
| Al      | 0 | 0 | 0.5    | 0.07  | 3b   |
| Mn      | 0 | 0 | 0.5    | 0.1   | 3b   |
| O       | 0 | 0 | 0.2423 | 1     | 6c   |

Figure 5.4 shows the X-ray diffraction patterns (XRD) of the NFAM-8155 cathode material and the difference pattern data after Rietveld analysis. It is observed that the cathode material is  $\alpha$ -NaFeO<sub>2</sub>-type (space group R-3m) and has a single phase structure with the chemical name Li<sub>0.992</sub> Ni<sub>0.0072</sub> Fe<sub>0.0008</sub> (Ni<sub>0.9</sub> Fe<sub>0.1</sub>)O<sub>2</sub> (COD ID: 1529125). Here, (006)/(012) and (018)/(110) peaks reveal that the obtained structure has high crystallinity, good hexagonal order and well-defined layered structure. The ratio of I(003)/I(104) is 1.21, indicating that the Li/Ni mixture is less. Table 5.5 shows the structural parameters of NFAM-8155 cathode material by Rietveld analysis. Goodness of fit value of Rietveld analysis is 2.33. About 7.8% of nickel atoms replaced lithium atoms in the 3a region, while about 0.4% of iron atoms were located in this

region. The lattice parameters a, b, c and volume are 2.89024 Å, 2.89024 Å, 14.32804 Å and 103.654 Å<sup>3</sup>, respectively.

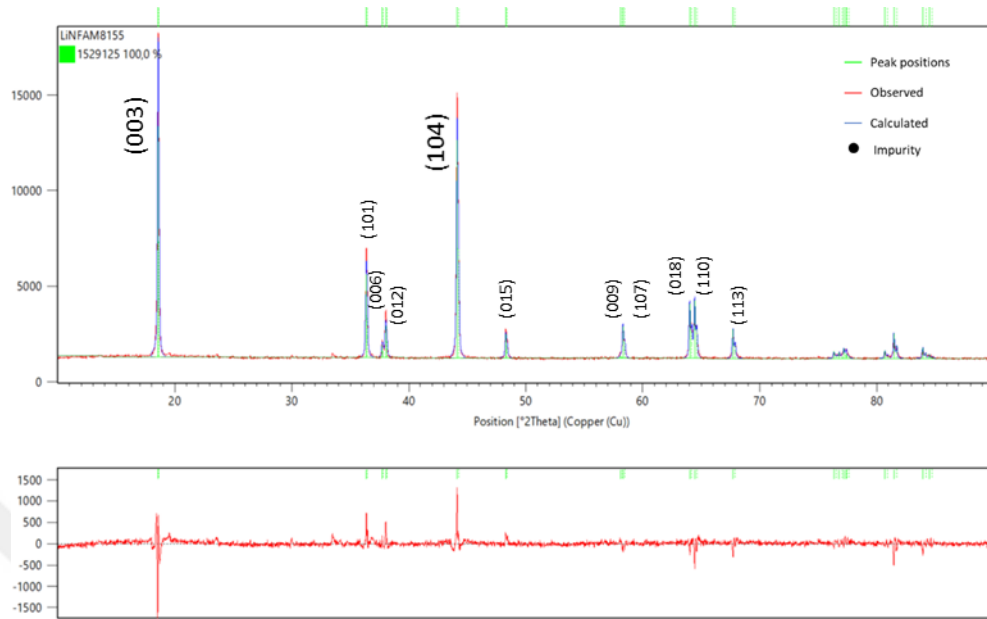


**Figure 5.4:** XRD analyses with difference pattern of NFAM-8155.

**Table 5.5 :** Rietveld analysis and structural parameters of NFAM-8155.

| Element | x | y | z      | Occ.   | Site |
|---------|---|---|--------|--------|------|
| Li      | 0 | 0 | 0      | 0.9396 | 3a   |
| Ni      | 0 | 0 | 0      | 0.06   | 3a   |
| Fe      | 0 | 0 | 0      | 0.0004 | 3a   |
| Li      | 0 | 0 | 0.5    | 0.0604 | 3b   |
| Ni      | 0 | 0 | 0.5    | 0.77   | 3b   |
| Fe      | 0 | 0 | 0.5    | 0.0996 | 3b   |
| Al      | 0 | 0 | 0.5    | 0.03   | 3b   |
| Mn      | 0 | 0 | 0.5    | 0.05   | 3b   |
| O       | 0 | 0 | 0.2423 | 1      | 6c   |

When the X-ray diffractions of the NFAM-8155 and NFAM-6211 cathode materials are first analysed, it can be said that although there is less nickel in the NFAM-6211 sample, there is more Li/Ni mixture. However, after Rietveld analysis, it is seen that the reason for this is the presence of iron in the 3b regions and therefore the diffraction intensity is more intense in this direction. Looking at the lattice parameters and volume values, it is seen that NFAM-6211 has larger lattice parameters and volume. This is due to the enlargement of the crystal structure by iron atoms as explained before. In general, it is thought that nickel and iron atoms are located at site 3a in both structures and therefore can significantly reduce the electrochemical performance of the battery cell. Nickel and iron atoms at these sites may prevent the diffusion of lithium ions,

leading to losses in the first discharge capacity. The schematic representation of the structures is drawn with VESTA and shown in Figure 5.5.

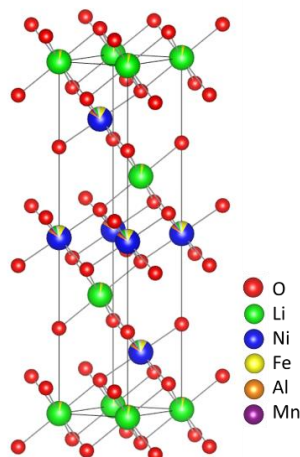


**Figure 5.5:** Schematic structure of NFAM (drawn by VESTA).

### 5.3 Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectrometry (SEM/EDS) Analysis

Figure 5.6 shows the scanning electron microscopy/energy-dispersive x-ray spectrometry (SEM/EDS) analyses of NFAM-6211 samples. When examined morphologically, as seen in Figure 5.6(a), it is seen that the agglomerated particles are 10 to 15 micrometres in average at 5000x magnification. SEM images at 1000x magnification are given in Figure 5.6(b). Morphologically, it is seen that the synthesised powders are planar or flower-like agglomerated by the aggregation of primary particles consisting of a few micrometres. This is far from the desired spherical morphology. Therefore, the powders cannot be more dense because they are not in a structure where spherical morphology is dominant, and this significantly negatively affects the battery performance of the active material.

Figure 5.6(c) and Figure 5.6(d) show the distribution of O, Ni, Fe, Mn, Al, and Mn metals in the particles, respectively. While it can be said that the metals are generally homogeneously distributed at 5000x and 1000x magnification, it is seen that aluminium is more concentrated in some regions and is much more heterogeneous than other metals.

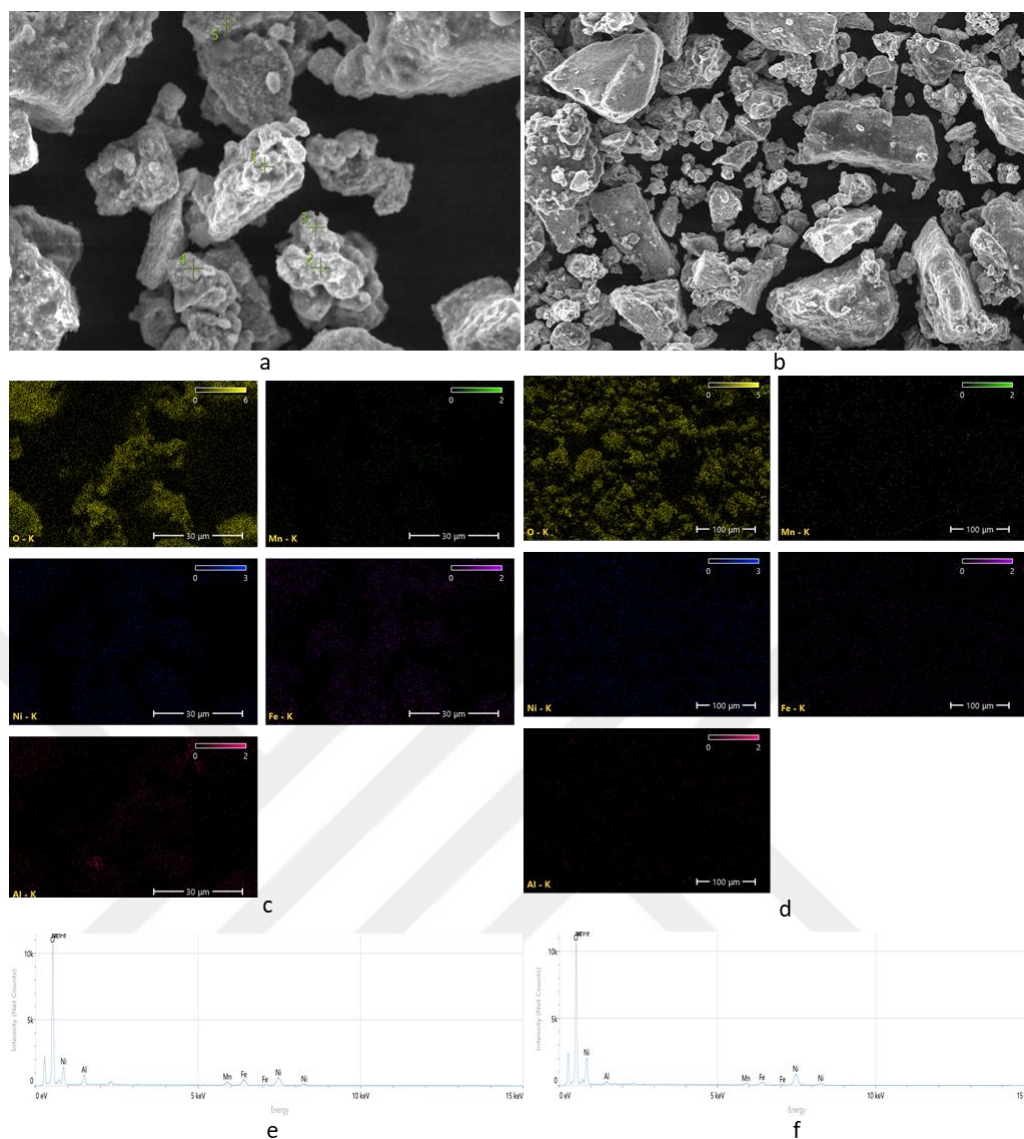


**Figure 5.6:** NFAM-6211 SEM results magnification of a) 5000x b) 1000x, EDS propagation map at magnification of c) 5000x d) 1000x, EDS spectrum data at magnification of e) 5000x f) 1000x.

**Table 5.6:** Atomic and weight percentages of the elements at 5000x magnifications for NFAM-6211.

| Element | Atomic % | Atomic % Error | Weight % | Weight % Error | Net Counts |
|---------|----------|----------------|----------|----------------|------------|
| O       | 67,4     | 0,5            | 38,2     | 0,3            | 53 168     |
| Al      | 4,4      | 0,1            | 4,2      | 0,1            | 5 600      |
| Mn      | 3,4      | 0,2            | 6,7      | 0,4            | 3 288      |
| Fe      | 7,1      | 0,2            | 14,0     | 0,4            | 6 446      |
| Ni      | 17,8     | 0,4            | 36,9     | 0,8            | 10 025     |

**Table 5.7:** Atomic and weight percentages of the elements at 1000x magnifications for NFAM-6211.

| Element | Atomic % | Atomic %<br>Error | Weight % | Weight %<br>Error | Net Counts |
|---------|----------|-------------------|----------|-------------------|------------|
| O       | 76,8     | 0,5               | 50,4     | 0,4               | 66 223     |
| Al      | 4,0      | 0,1               | 4,5      | 0,1               | 5 564      |
| Mn      | 2,2      | 0,2               | 5,0      | 0,4               | 2 125      |
| Fe      | 5,2      | 0,2               | 11,8     | 0,5               | 4 646      |
| Ni      | 11,7     | 0,3               | 28,3     | 0,8               | 6 629      |

Figure 5.7 shows the scanning electron microscopy/energy-dispersive x-ray spectrometry (SEM/EDS) analyses of NFAM-6211 samples. As seen in Figure 5.7(a), it is seen that the secondary particles formed by the aggregation of particles of a few micrometres in size at 5000x magnification are 10 to 15 micrometres on average. Figure 5.7(b) shows the SEM images at 1000x magnification. It is seen that NFAM-8155 has a more spherical morphology than NFAM-6211. Figure 5.7(c) and Figure 5.7(d) show the distribution of O, Ni, Fe, Mn, Mn, and Al metals in the particles, respectively. It is seen that NFAM-8155 has a more homogeneous elemental distribution compared to NFAM-6211. However, although aluminium shows better homogeneity in NFAM-8155, it is still not as well-defined as the other elements.

Figure 5.7(e) and Figure 5.7(f) show the EDS spectra of the elements at the respective magnifications. The peaks at about 1.7 kV, which appear much smaller, and 2.3 kV belong to the  $K_{\alpha 1,2}$  peak of Si and S, respectively. Table 5.8 and Table 5.9 give the data of the elements at 5000 and 1000 magnification, respectively, with their atomic and weight percentages. It can be seen at both magnifications that NFAM-8155 is closer to the desired composition and much more consistent in terms of distribution than NFAM-6211.

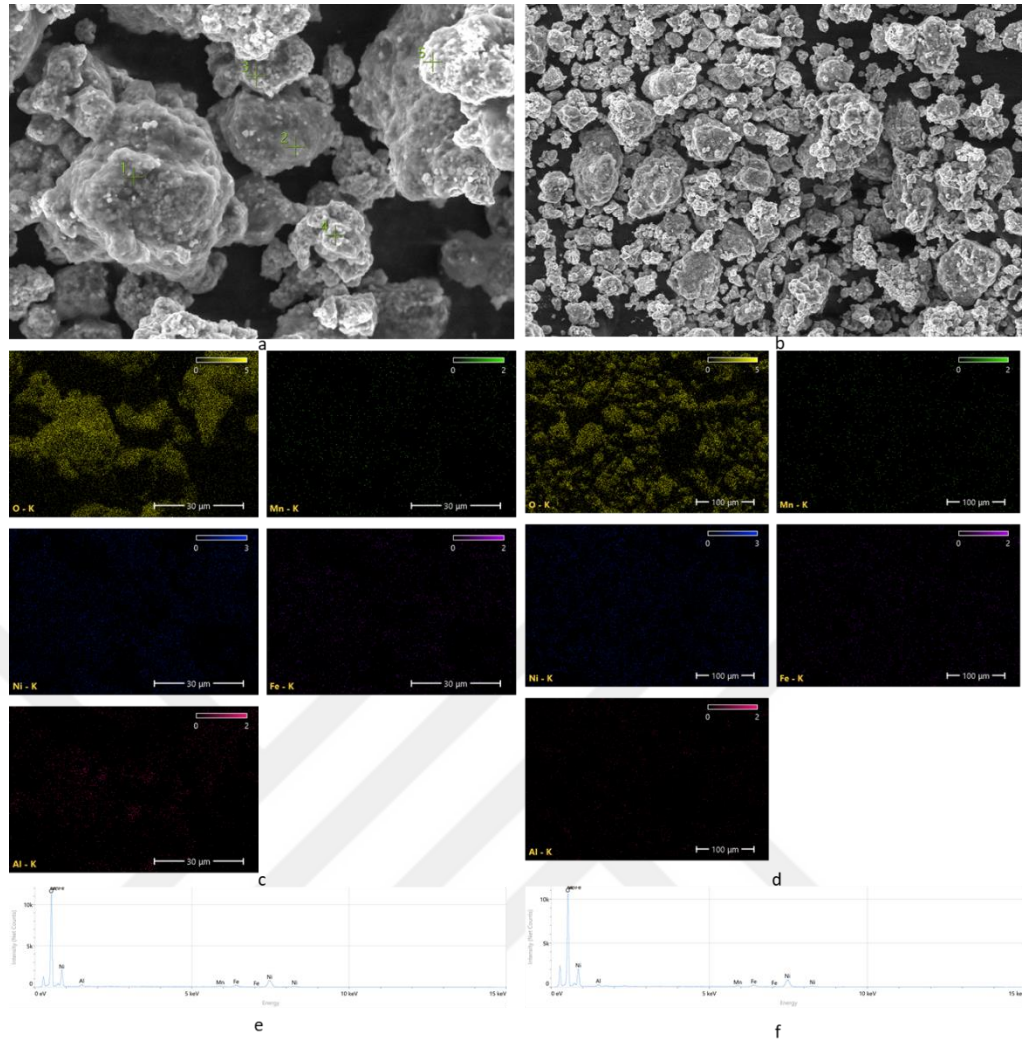


**Figure 5.7:** NFAM-8155 SEM results magnification of a) 5000x b) 1000x, EDS propagation map at magnification of c) 5000x d) 1000x, EDS spectrum data at magnification of e) 5000x f) 1000x.

**Table 5.8:** Atomic and weight percentages of the elements at 5000x magnifications for NFAM-8155.

| Element | Atomic % | Atomic % Error | Weight % | Weight % Error | Net Counts |
|---------|----------|----------------|----------|----------------|------------|
| O       | 71,5     | 0,5            | 41,5     | 0,3            | 58 485     |
| Al      | 1,4      | 0,1            | 1,4      | 0,1            | 1 799      |
| Mn      | 1,6      | 0,2            | 3,2      | 0,3            | 1 639      |
| Fe      | 2,8      | 0,2            | 5,6      | 0,3            | 2 735      |
| Ni      | 22,7     | 0,4            | 48,4     | 0,8            | 13 316     |

**Table 5.9:** Atomic and weight percentages of the elements at 1000x magnifications for NFAM-8155.

| Element | Atomic % | Atomic %<br>Error | Weight % | Weight %<br>Error | Net<br>Counts |
|---------|----------|-------------------|----------|-------------------|---------------|
| O       | 70,3     | 0,5               | 40,0     | 0,3               | 53 410        |
| Al      | 1,4      | 0,1               | 1,4      | 0,1               | 1 708         |
| Mn      | 1,4      | 0,2               | 2,8      | 0,3               | 1 389         |
| Fe      | 3,1      | 0,2               | 6,1      | 0,4               | 2 893         |
| Ni      | 23,8     | 0,4               | 49,7     | 0,9               | 13 083        |

## 6. CONCLUSIONS

In this study, NFAM-6211 and NFAM-8155 cathode materials were synthesised by co-precipitation method. Based on the XRF analysis performed for elemental analysis, the aluminium content in the cathode materials was observed to be relatively lower than the targeted composition. Based on the XRF results during the production process, it was observed that washing with centrifuge caused a lot of impurity to remain in the structure and it was more accurate to wash with filter paper. XRD and Rietveld analyses showed that a layered structure with an acceptable Li/Ni mixture was obtained for both cathode materials. In the calcination step, it was observed that the Li/Ni mixture was much higher when oxygen was blown into the furnace atmosphere and the reason for this was the oxygen loss in the structure. According to Rietveld analysis, it was observed that iron atoms replaced lithium atoms in both cathode materials and this situation increased with increasing iron content. SEM analyses showed that the samples obtained were more flat-like in morphology and the secondary particles grew more spherical on the surface of the agglomerations in this morphology. The average grain size for both samples obtained is around 10 micrometres. In the EDS results, the distribution of the elements was examined for both samples and it was observed that the aluminium distribution of sample NFAM-6211 was more heterogeneous than that of sample NFAM-8155. Other than that, nickel, manganese and iron metals are homogeneously distributed for both samples. In addition to this, it was analysed that more than the targeted oxidation of the structure occurred with the external oxygen gas blowing during calcination, so there were deviations in terms of composition at both 5000 and 1000 magnifications. It is thought that the  $K\alpha$  peak belonging to the sulfur atom, which also appears in XRF and XRD analyses, belongs to the sulfur atom from the precursor materials and will affect the electrochemical performance. The produced samples were used as active material to obtain slurry and used as cathode in CR 2032 button battery cell. However, as a result of the galvanostatic charge and discharge test, successful results have not yet been obtained due to precipitation during the slurry preparation process, coating defects and problems during battery assembly, and studies on the subject are ongoing.



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