

Article Processing Dates: Received on 2024-05-06, Reviewed on 2024-06-21, Revised on 2024-08-09, Accepted on 2024-08-10 and Available online on 2024-08-30

# Mechanical processing with solid-state of supercapacitor materials: a review of high energy milling and highvelocity particle methods

Mahruri Arif Wicaksono<sup>1,2</sup>, Bambang Suharno<sup>1\*</sup>, Widi Astuti<sup>2</sup>, Yayat Iman Supriyatna<sup>2</sup>, Slamet Sumardi<sup>2</sup>

<sup>1</sup>Department of Metallurgy and Materials Engineering, University of Indonesia, Depok City, 16425, Indonesia

<sup>2</sup>Research Center of Mining Technology, National Research and Innovation Agency, Lampung, 35361, Indonesia

\*Corresponding author: suharno@metal.ui.ac.id

### Abstract

Supercapacitors have emerged as a crucial energy storage technology, bridging the gap between traditional capacitors and batteries. The performance of supercapacitors is heavily dependent on the properties of the electrode materials used. Mechanical processing methods, particularly High Energy Milling (HEM) and High-Velocity Particle (HVP) methods have shown great promise in enhancing the physical and electrochemical properties of supercapacitor materials. This review explores the fundamental principles, mechanisms, and recent advancements in HEM and HVP techniques for the synthesis and modification of supercapacitor materials. High energy milling, including ballmill and attritor milling, facilitates particle size reduction, increased surface area, and the creation of nanostructures, leading to improved capacitance and energy density. High velocity particle methods, such as cold spraying and thermal spraying, enable the deposition of uniform and dense coatings, enhancing conductivity and stability. The review also discusses the impact of process parameters on material properties, the challenges faced in scaling up these techniques, and the potential future directions for research. By providing a comprehensive overview of these mechanical processing methods, this paper aims to highlight their significance and potential in advancing supercapacitor technology.

## **Keywords:**

Supercapacitor, mechanical processing, solid-state materials, High Energy Milling (HEM), High-Velocity Particle (HVP) methods.

## 1 Introduction

Solid-state supercapacitor engineering of the homogenization process in a planetary ballmill involves the use of kinetic energy to break materials into smaller particles. In a planetary ballmill, the fragmentation and homogenisation process is based on the principle of rotational movement of the vial which causes the balls inside to collide with each other resulting in kinetic energy being transferred to the material resulting in fragmentation and homogenisation [1]. In the simulation process, it is shown that the kinetic parameters of the milling process are significantly influenced by the rotational speed ( $\omega$ ) and the vial- to-disc speed ratio ( $\omega/\omega$ ), under optimal operating conditions obtained at  $\omega$  = 800 rpm [2]. Thermal conditions involve the application of kinetic energy with the addition of heat to enhance the process where thermal processing can change the properties of a material or facilitate chemical reactions that will occur [3].

In addition to using a planetary ballmill, the fragmentation and homogenisation process can also use the high-velocity collision method. High-velocity collision is one method in material engineering and manufacturing, for example, such as High Velocity Oxygen Fuel (HVOF) with a high velocity of approximately 975 m/s exceeding the speed of sound so that it can produce 10-1 µm particle fragmentation [4]. In the HVOF process, the kinetic energy of particles is more important than temperature because this method uses very high collision energy to produce solid layers at low temperatures [5]. Fluidised metallurgical powder feedstock is fed into or upstream of the nozzle (hopper), where it is accelerated by the gas flow and strikes the substrate at high velocities ranging between 200 m/s and 1200 m/s depending on the choice of process and spray parameters until it can reach temperatures of 800°C [6]. In processing the manufacture of batteries or supercapacitors using mechanical methods to perform homogeneity of Li, Ni, Mn and Co power storage alloy materials with solid-state. The solid-state process is divided into several parts such as wet mixing methods (high shear mixing, wet ball milling, ultrasonic mixing, magnetic stirring) and then dry mixing methods (dry mixing methods, extrusion, melt-granulation) [7].

In addition to mechanical processes, there are also chemical processes by adding chemical elements as reaction catalysts. As in the processing of NMC-Nd supercapacitors using several methods such as sol-gel, solid-state, co-precipitation, hydrothermal, and combustion. Currently, the process of making NMC energy storage uses a solid-state method, but there are obstacles when using the solid-state ball mill method, the formation process takes a long time even up to days [8].

The sol-gel process is typically performed in small batches, which can be difficult to scale up to large volumes. This requires significant modifications to the equipment and process conditions to ensure consistent quality and efficiency. Industrial-scale production requires significant investments in equipment and labor. The process must be efficient to ensure cost-effectiveness and minimize environmental impact [9]. Hydrothermal methods require precise control over pressure to ensure consistent product quality. This can be challenging to maintain on an industrial scale, where equipment must be designed to handle large volumes and maintain consistent conditions. Hydrothermal methods are often performed in small batches, which can be difficult to scale up to large volumes. This requires significant modifications to the equipment and process conditions to ensure consistent quality and efficiency [10]. The manufacture of LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> (LNMC) cathode material for cathode Li-ion batteries has been carried out through the hydrothermal method [9]. LNMC material was chosen because it has many advantages such as abundant material availability, low cost, high capacity and superior power storage performance [11].

In review, solid-state methods are often used in the manufacture of anode and cathode materials for batteries because they are able to produce materials with high purity and good particle distribution. Ball milling process, the roller mill type provides gentler grinding and is more efficient in terms of energy compared to other types of ball mills. Ni<sub>0.64</sub>Mn<sub>0.2</sub>Co<sub>0.16</sub>O<sub>2</sub> with the addition of Neodymium Oxide (Nd<sub>2</sub>O<sub>3</sub>) aims to improve electrode properties such as thermal stability and conductivity. In the coin punch cell type power storage prototype after adding Nd<sub>2</sub>O<sub>3</sub>, it will increase the resistance value by 17.5% at 300 cycles [12]. The use of the solid-state method in making power storage materials is considered the simplest and easiest method because it does not require a lot of chemicals, can be produced on a large scale, and is very efficient if a failure occurs in a process because the material can be reused. This method is particularly useful for the development of solid-state batteries, where the solid electrolyte offers several advantages over traditional lithium-ion batteries,

including reduced flammability and the elimination of environmentally harmful compounds [13].

The solid-state process in supercapacitor manufacturing is rapidly emerging as a game-changer within the energy storage industry. This innovative approach offers a myriad of benefits, notably its ability to significantly reduce waste and save manufacturing time. Unlike traditional liquid-based methods, the solid-state process minimizes the use of hazardous chemicals and materials, leading to a more environmentally friendly production cycle [14]. Additionally, this method streamlines various manufacturing steps, enhancing efficiency and productivity. In an era where sustainability and operational efficiency are paramount, the solid-state process presents a compelling solution. By eliminating the need for solvents and reducing the complexity of the manufacturing workflow, it not only cuts down on production time but also decreases the overall cost [15]. This shift not only benefits manufacturers but also aligns with global efforts to reduce environmental impact and promote greener technologies. This article delves into the advantages of the solid-state process in supercapacitor manufacturing, exploring how it revolutionizes the production landscape. We will examine the specific ways this process contributes to waste reduction, time savings, and overall cost efficiency, underscoring its potential to set new standards in the industry [16].

The use of the solid-state method in manufacturing prioritizes the principles of physical processes, resulting in products with exceptional thermal conductivity. This approach ensures that materials achieve a perfectly homogeneous structure, facilitating the formation of strong, solid bonds between particles. Unlike traditional methods, which may rely on solvents or involve multiple stages that can introduce impurities or inconsistencies, the solid-state method provides a streamlined process that enhances material integrity and performance [17].

Thermal conductivity is a critical property for a wide range of applications, from electronics to energy storage systems. By ensuring that the material's structure is uniform and free from defects, the solid-state method enhances heat transfer capabilities, making it ideal for producing high-performance components [18]. The ability to create materials with superior thermal properties not only improves product efficiency but also extends the lifespan of the components by mitigating issues related to thermal stress and degradation. This article explores the solid-state method's role in advancing manufacturing techniques, particularly its impact on thermal conductivity [19]. We will delve into the physical principles underpinning this method, highlight the benefits of achieving a homogeneous material structure, and discuss the various applications where these improvements can be most effectively leveraged. Through this examination, we aim to underscore the transformative potential of the solid-state method in producing high-quality, thermally conductive products.

### 2 Materials of Supercapacitor

Extensive review for power storage cathode materials such as Lithium Cobalt Oxide (LCO), Lithium Ferrous Phosphate (LFP), Lithium-Titanate Oxide (LTO), Lithium Manganese Oxide (LMO) and recently lithium nickel manganese aluminum oxide (NCA) and lithium nickel manganese cobalt oxide (NMC) [8] (Fig. 1). By comparing in terms of cost, lifetime, performance, safety, specific energy, and material power. Among them, NMC has the best overall performance (Tabel 1). The diversity in NMC materials is due to the different compositions of nickel, cobalt, and manganese to form  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC333), LiNi0.  $4\text{Co}_{0.4}\text{Mn}_{0.2}\text{O}_2$  (NMC442),  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  (NMC532),  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) and  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811) [14] (Tabel 2).



Fig. 1. Comparison of various types of cathodes [20].

Currently the use of materials for supercapacitors there are several types of materials used for electrodes from nature and metal oxide type electrodes and electrolytes. For electrodes, materials such as Activated Carbon (AC), Carbon Fibre-Cloth (AFC), Carbide-Derived Carbon (CDC), carbon aerogel, graphite, graphene and Carbon Nanotubes (CNTs) [21] (Fig. 2). Then for metal oxide that can be used as supercapacitor electrodes such as RuO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, IrO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and CuO, Fe<sub>2</sub>O<sub>3</sub>/Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>/NiCo<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>/ZnFe<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>/NiCo<sub>2</sub>O<sub>4</sub>, ZnO/ZnFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>. Then for the electrolyte used, which is like the Table 3.

### 3 Results and Discussion

#### 3.1 Power Storage Manufacturing Process

The synthesis method in the power storage electrode manufacturing process greatly affects the stability such as the morphology and composition of the power storage. The process method for manufacturing supercapacitors can vary depending on the type of supercapacitor (e.g., Electrochemical Double-Layer Capacitors (EDLCs) or pseudocapacitors), the materials used and the desired specifications. Here's a generalized overview of the process method for manufacturing supercapacitors (Tabel 4).

Cathode type	Ratios (R) or cell designation (S)	Manufacturer	EV model	Energy (useable) (kWh)	Range* (km)
Li-nickel	532 (R)	Nissan	Nissan Leaf e+	62	385
manganese		CATL	Peugeot e 208, Opel	50 (46)	349
cobalt oxide			Corsa-e		336
		Envision AESC	Nissan Leaf	39.5 (36)	270
	333 (R)	Samsung SDI	Volkswagen e-Golf	35.8 (32)	232
	721 (R)	LG Chem	Renault ZOE	54.7 (52)	232
		SK innovation	Volkswagen ID.4 Pro	82 (77)	467
	622 (R)	Samsung SDI	BMW i3	42.2 (37.9)	293
		SK innovation	Kia e-Soul,	67.5 (64)	451
			Kia e-Niro		454
			Volkswagen e-UP, Seat	36.8 (32.3)	260
			Mii Electric, Skoda		256
			CITIGo-e		265
			Hyundai Ioniq-e	40.4 (38.3)	310
			Hyundai Kons-e	67.5 (64)	447
			Mercedes Benz EQC	85 (80)	417
		LG Chem	Porche Taycan, Jaguar I-	93.4 (83.7),	333
			Pace	90 (84.7)	470
			Audi e-tron 55 Quattro	95 (86.5)	402
			Chevrolet Bolt	68	417
	811 (R)	-	Jeep Avenger	54 (50.8)	346
			Vauxhall Astra Sports		346
			Tourer		
			DS 3 E-Tense		346

Table 1. NMC cathode used in electric cars and its main characteristics [14]

Table 2. NMC622 and NMC811 were synthesised using different methods and their electrochemical performance [8]

			0			1 6 3	
Ni-rich NMC	Synthesis route	Current	Voltage Initial discharge Cycle no	Cycle no	Final discharge	Capacity	
		density	range (V)	capacity (mAhg <sup>-1</sup> )	Cycle IIO.	capacity (mAhg <sup>-1</sup> )	retention
NMC622	Solid state reaction	0.5 C	2.8 - 4.3	153.8	100	152.4	99.1 %
	Solid state reaction	1.0 C	2.8 - 4.3	160.8	40	150.6	93.7 %
	Co-precipitation	0.05 C	3.0-4.3	210.0	100	197.4	94.0 %
	Hydrothermal	0.5 C	2.8 - 4.6	185.0	50	149.9	81.0 %
	Combustion	1.0 C	2.8 - 4.3	170.0	30	166.9	98.2 %
NMC811	Sol-gel	0.5 C	2.5 - 4.3	200.0	50	164.4	82.2 %
	Sol-gel	1.0 C	2.7 - 4.3	176.3	100	139.3	79.0 %
	Solid state reaction	2.0 C	2.8 - 4.3	125.2	500	13.7	10.9 %
	Hydrothermal	1.0 C	2.8 - 4.3	190.0	200	163.8	86.2 %
	Co-precipitation	1.0 C	3.0-4.3	172.0	100	126.6	73.6 %
	Co-precipitation	0.2 C	2.8 - 4.3	188.7	184	150.9	80 %



Table 3 Material properties of electrode and electrolyte variations of supercapacitors $12^{\circ}$	21

Material	Density (g/cm <sup>3</sup> )	Electrolyte	F/g	F/cm <sup>3</sup>
Carbon cloth	0.35	KOH organic	200	70
		-	100	35
Activated carbon	0.7	KOH organic	160	112
			100	70
Aerogel carbon	0.6	KOH organic	50-75	84
			100-125	
Particulate carbon from SiC	0.7	KOH organic	175	122
Particulate carbon from TiC	0.5	KOH organic	220	110
			120	60
Anhydrous RuO <sub>2</sub>	2.7	Sulphuric acid	150	405
Hydrous RuO <sub>2</sub>	2.0	Sulphuric acid	650	1300
Doped conducting polymer	0.7	Organic	450	315

Method

Synthesis variation sol-gel, electro-polymerization, hydrothermal, co-precipitation, chemical vapor deposition, direct coating, vacuum filtration, de-alloying, microwave auxiliary, in situ polymerization, electro-spinning, silar, carbonization, dipping and drying methods [24].





NMC Co-precipitation process [30]



## 3.2 Solid State Method Supercapacitor Process

Solid-state methods involve the formation of supercapacitor materials from semiconductor materials that have been treated in a solid state. This process involves the use of technologies such as sintering, calcination, or direct chemical reactions to produce materials with complex pore structures and high capacitance. These semiconductor materials can then be used as electrodes in supercapacitors.

## 3.2.1 Milling Process

In solid-state processes, the use of planetary ball mills is designed to break down large particles into smaller sizes. This is very important in various applications, such as in the processing of agricultural raw materials, powder metallurgy, mining materials processing, and chemical. technology. This equipment can break down large particles to nanometre sizes that other methods cannot achieve. In addition to breaking down, planetary ball mills can also be used to combine different particles into one homogeneous mixture. This is particularly useful in the pharmaceutical, chemical, materials engineering, mining and food industries for further processing [38] (Fig. 3).

Simulations using the Discrete Element Method (DEM) to predict the motion of milling objects in a planetary ball mill. Changes in the impact frequency and energy of milling objects as a function of process conditions will be studied using various simulations. The accuracy of parameter calculations and processing efficiency in planetary ball mills can be improved by using 3D computer models (Fig. 4).



Fig. 4. Calculated motion trajectory of a milling body in the x, y and z planes [39].

In material synthesis, the latest method uses high-temperature and High-Pressure Planetary Ball Milling (HTPRM). HTPRM allows the mechanosynthesis of materials at fully controlled temperatures of up to 450°C and pressures of up to 100 bar of hydrogen. An example of this application is the magnesium hydride synthesis process. The synthesis is carried out at controlled temperatures (Room Temperature (RT), 100, 150, 200, 250, 300, and 325°C) while refining in a planetary ballmill under hydrogen pressure (>50 bar) [40] (Fig. 5).

Air jet milling effectively reduces particle size from a range of 20-100  $\mu$ m to less than 10  $\mu$ m. In this micronisation method, a high-velocity compressed air stream is injected into the chamber

where the initial raw material is fed by a feeder controlled by the feeder. The air is introduced through a specially designed fluid inlet to create a sonic or supersonic airflow. High-speed collisions between the raw particles lead to effective crushing of the feed into smaller particles. High-pressure homogenisation is a highenergy process where particle size reduction is achieved by repeatedly cycling up to 200 cycles more at high speed, around 500 m/s and 10-15 bar pressure [41] (Fig. 6).



Fig. 5. SEM images of Mg powder: a) Raw material b) RT, c) 100°C, d) 150°C, e) 200°C, f) 250°C, g) 300°C, and h) 325°C [40].



Fig. 6. Schematic diagram of high-pressure homogenisation process [41].

### **3.2.2 High Collision Particle**

High-pressure particle coating technique is a solid form deposition technique for almost all types of metals, alloys and powders. This method is through the collision of particles with high velocity pressure (helium, nitrogen, and air) at lower temperatures or high temperatures [42]. The powder particles used for this technique remain solid during the coating process. The coating is formed by metallurgical bonding and mechanical interlocking. This process is generally divided into two categories: room temperature and High-Pressure Thermal Spray Process (HPCSP) (greater than 10 bar or 800-1400 m/s) and room temperature and Low-Pressure Thermal Spray Process (LPCSP) (less than 10 bar or 300-600 m/s) [43] (Fig. 7).

With supersonic flow, the powder particles hit the substrate with greater speed and develop a coating with excellent cohesive and adhesive properties. In LPCSP, the gas pressure comes from the air. Initial mixing of the feedstock powder and carrier gas does not occur because the powder feeder is placed in the convergence region of the CD nozzle. However, the LPCSP method has poor cohesive properties compared to the HPCSP coating [45] (Fig. 8).



Fig. 7. Schematic representation of the high-speed particle process [44].



Fig. 8. Schematic bonding particle in the substrate [46].

The cold spray technique is a method to create coatings by using particles associated with high velocities that convert their kinetic energy into plastic deformation, strain and finally heat when colliding with sub-layers or previously deposited particles. Since there is no melting of the particles the result of the coating technique has lower oxidation and residual stress [47] (Fig. 9).

To create coatings, injection gas dynamic spraying techniques combine coarser, non-plastically mouldable hard particles such as ceramics and tungsten with smaller ductile particles. To develop particle bonds with other particles and the substrate, all processes depend on the transformation of the kinetic energy of the particles. Particle kinetic energy and momentum in layer development must be transformed into other forms of energy through plastic deformation, cavity consolidation, particle rotation, plastic strain and finally heat. If all the incident kinetic energy is converted into heat and plastic strain energy the particles will bounce which will result in elastic collisions.





#### 3.2.3 NMC811 Supercapacitor

In the synthesis process of NMC811 by reducing the particle size of metal oxides such as MnO, NiO, and CoO, which are precursor materials used in the synthesis of NMC811 cathode materials, can improve its electrical properties. This is because the smaller particle size leads to shorter lithium-ion diffusion pathways and higher surface area, resulting in better electrochemical performance. The solid-state synthesis method is commonly used in the manufacturing of NMC811 cathode materials, as it allows for better control over the particle size and homogeneity of the final product. In this process, the precursor metal oxides are mixed in the desired stoichiometric ratios and subjected to high-temperature calcination, typically between 700°C and 1000°C, under an oxidizing atmosphere [49].

To reduce the particle size and achieve finer NMC811 particles, various techniques are employed, such as ball milling,

co-precipitation, and sol-gel synthesis. Ball milling is a mechanical process that involves grinding the precursor materials using high-energy milling balls, resulting in a reduction in particle size and improved homogeneity [50]. Researchers have demonstrated that reducing the particle size of NMC811 cathode materials can significantly improve their electrochemical performance. For instance, a study by Liu et al. [51] reported that NMC811 cathode materials with a particle size of around 200 nm exhibited higher discharge capacities and better rate capabilities compared to larger particles (>1 µm). Another study by Zuo et al. [52] revealed that NMC811 cathode materials with particle sizes ranging from 100 nm to 500 nm showed improved cycling stability and rate performance compared to larger particles. The authors attributed these improvements to the reduced lithium-ion diffusion distances and increased electrode-electrolyte contact area in smaller particles.

The mass of nickel oxalate, manganese oxalate, and the cobalt oxalate needed to make the NMC811 material is calculated by mole ratio Ni:Mn:Co = 8:1:1. Nickel oxalate, manganese oxalate, and cobalt oxalate are mixed until smooth. Next is nickel oxalate, manganese oxalate, and cobalt oxalate were calcined at 500°C for 6 hours. After that, the lithium hydroxide (LiOH·H<sub>2</sub>O) required is calculated with a ratio of NMC:Li = 1:1.1. NMC materials are mixed with lithium hydroxide (LiOH·H<sub>2</sub>O) until smooth. The LiNMC material was sintered at a temperature of 800°C for 15 hours. The sintered LiNMC material is ground using a mortar and pestle [53] (Fig. 10).



Fig. 10. SEM images of the NMC811 [54].

### 3.2.4 NMC811 Supercapacitor Dopand REE's

The increasing demand for efficient lithium-ion batteries to power vehicles and energy storage requires improvements in the properties of cathode materials. In the LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> series battery (NMC622), the cathode material is doped with selected rare earth metal ions (La, Nd, Eu) at various concentrations (0.5-1.5 mol%) [55]. Compared with undoped cathode materials, doped cathode materials have different lattice characteristics and can improve electrochemical performance such as capacity, stability and diffusion coefficient of lithium ions. For example, in the research conducted by Ding et al. (2007), rare earth element doping improved the discharge capacity and cycle performance of  $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  (La, Ce, Pr) [56] (Tabel 5).

The study on the effects of La-doping on LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> material revealed a significant improvement in cyclic stability, which increased from 74.3% to 95.2% following the doping process. In addition, the La (1.0)-doped material has a greater capacity than the pure material [57]. Compared with the pure material, LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> doped with a small amount of Nd has lower charge-discharge polarisation and lower charge transfer resistance [58]. Meanwhile, Eu-doped LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> has

excellent discharge capacity, cycle stability, better rate performance and lower charge transfer resistance than pure material [59] (Fig. 11).

Table 5. Initial charge-discharge capacity and coulomb efficiency for cathode materials at 0.1C in the voltage range 3.0-4.3 V vs. Li/Li+ [60]

	Initial charge	Initial discharge	Coulombic
Cathode material	capacity	capacity	efficiency
	$(mAh/g^{-1})$	$(mAh/g^{-1})$	(%)
NMC622 pristine	183.4	137.2	74.8
NMC622-La0.5	197.6	151.1	76.5
NMC622-La1.0	187.5	151.8	81.0
NMC622-La1.5	184.8	150.0	81.2
NMC622-Nd0.5	193.3	160.1	82.8
NMC622-Nd1.0	185.3	151.8	81.9
NMC622-Nd1.5	169.2	149.9	88.6
NMC622-Eu0.5	185.6	153.1	82.5
NMC622 pristine	183.4	137.2	74.8
NMC622-La0.5	197.6	151.1	76.5



Fig. 11. SEM images of the NMC811 dopand Nd<sub>2</sub>O<sub>3</sub> [61].

### 4 Conclusion

Selecting suitable precursor materials with high purity and compatibility is fundamental. Precursors are often selected based on their ability to form the desired superconducting phase. Solidstate synthesis methods, including solid-state reactions and mechanical alloying, are essential for converting precursor materials into superconducting compounds. These processes drive chemical reactivity and phase formation in mechanical grinding and mixing techniques are used to homogenize the precursor powder and ensure uniform distribution of its constituent elements. This facilitates the formation of a homogeneous superconducting phase.

## Acknowledgments

The authors express their sincere appreciation to the Department of Metallurgy and Materials Engineering, Faculty of

Engineering, University of Indonesia and the National Research and Innovation Agency which has provided experimental settings and laboratory support which has made a significant contribution to completing this research.

#### References

- Broseghini, M., Gelisio, L., D'Incau, M., Ricardo, C. A., Pugno, N. M., & Scardi, P. (2016). Modeling of the planetary ball-milling process: The case study of ceramic powders. Journal of the European Ceramic Society, 36(9), 2205-2212.
- Chattopadhyay, P. P., Manna, I., Talapatra, S., & Pabi, S. K. (2001). A mathematical analysis of milling mechanics in a planetary ball mill. Materials Chemistry and Physics, 68(1-3), 85-94.
- 3. Baran, A., Knioła, M., Rogala, T., & Polanski, M. (2022). New horizon in mechanochemistry-high-temperature, high-

pressure mechanical synthesis in a planetary ball mill-with magnesium hydride synthesis as an example. International Journal of Hydrogen Energy, 47(82), 35003-35016.

- Vigneshkumar, M., Murugan, S. S., Varthanan, P. A., Gokilakrishnan, G., Gobikrishnan, N., & Pagutharivu, A. P. (2022, October). High velocity oxygen fuel coating for enhancing tribological behaviour of engineering metals. In AIP Conference Proceedings (Vol. 2527, No. 1). AIP Publishing.
- Bakan, E., Mauer, G., Sohn, Y. J., Koch, D., & Vaßen, R. (2017). Application of high-velocity oxygen-fuel (HVOF) spraying to the fabrication of Yb-silicate environmental barrier coatings. Coatings, 7(4), 55.
- Adaan-Nyiak, M. A., & Tiamiyu, A. A. (2023). Recent advances on bonding mechanism in cold spray process: A review of single-particle impact methods. Journal of Materials Research, 38(1), 69-95.
- Fernandez-Diaz, L., Castillo, J., Sasieta-Barrutia, E., Arnaiz, M., Cabello, M., Judez, X., & Villaverde, A. (2023). Mixing methods for solid state electrodes: techniques, fundamentals, recent advances, and perspectives. Chemical Engineering Journal, 464, 142469.
- Saaid, F. I., Kasim, M. F., Winie, T., Elong, K. A., Azahidi, A., Basri, N. D.,& Rusop, M. (2023). Ni-rich lithium nickel manganese cobalt oxide cathode materials: A review on the synthesis methods and their electrochemical performances. Heliyon.
- Ma, Q., Xu, Q., Tsai, C. L., Tietz, F., & Guillon, O. (2016). A Novel Sol–Gel Method for Large-Scale Production of Nanopowders: Preparation of Li<sub>1.5</sub>A<sub>10.5</sub>Ti<sub>1.5</sub> (PO<sub>4</sub>)<sub>3</sub> as an Example. Journal of the American Ceramic Society, 99(2), 410-414.
- 10. Ciriminna, R., & Pagliaro, M. (2022). Open challenges in sol-gel science and technology. Journal of Sol-Gel Science and Technology, 101(1), 29-36.
- Widiyandari, H., Sukmawati, A. N., Sutanto, H., Yudha, C., & Purwanto, A. (2019, February). Synthesis of LiNi<sub>0.8</sub>Mn<sub>0.1</sub>Co<sub>0.1</sub>O<sub>2</sub> cathode material by hydrothermal method for high energy density lithium ion Power Storage. In Journal of Physics: Conference Series (Vol. 1153, No. 1, p. 012074). IOP Publishing.
- Essehli, R., Parejiya, A., Muralidharan, N., Jafta, C. J., Amin, R., Dixit, M. B.,& Belharouak, I. (2022). Hydrothermal synthesis of Co-free NMA cathodes for high performance Li-ion batteries. Journal of Power Sources, 545, 231938.
- Jiang, M., Zhang, Q., Wu, X., Chen, Z., Danilov, D. L., Eichel, R. A., & Notten, P. H. (2020). Synthesis of Ni-rich layered-oxide nanomaterials with enhanced Li-ion diffusion pathways as high-rate cathodes for Li-ion batteries. ACS applied energy materials, 3(7), 6583-6590.
- Costa, R. S., Guedes, A., Pereira, A. M., & Pereira, C. (2020). Fabrication of all-solid-state textile supercapacitors based on industrial-grade multi-walled carbon nanotubes for enhanced energy storage. Journal of Materials Science, 55(23), 10121-10141.
- 15. Akin, M., & Zhou, X. (2022). Recent advances in solid-state supercapacitors: from emerging materials to advanced applications. International journal of energy research, 46(8), 10389-10452.
- Huang, C., Zhang, J., Young, N. P., Snaith, H. J., & Grant, P. S. (2016). Solid-state supercapacitors with rationally designed heterogeneous electrodes fabricated by large area spray processing for wearable energy storage applications. Scientific reports, 6(1), 25684.
- Wei, L. C., Ehrlich, L. E., Powell-Palm, M. J., Montgomery, C., Beuth, J., & Malen, J. A. (2018). Thermal conductivity of metal powders for powder bed additive manufacturing.

Additive Manufacturing, 21, 201-208.

- 18. Aksöz, S., Öztürk, E., & Maraşlı, N. (2013). The measurement of thermal conductivity variation with temperature for solid materials. Measurement, 46(1), 161-170.
- 19. Zhao, D., Qian, X., Gu, X., Jajja, S. A., & Yang, R. (2016). Measurement techniques for thermal conductivity and interfacial thermal conductance of bulk and thin film materials. Journal of Electronic Packaging, 138(4), 040802.
- 20. Schlem, R., Burmeister, C. F., Michalowski, P., Ohno, S., Dewald, G. F., Kwade, A., & Zeier, W. G. (2021). Energy storage materials for solid-state batteries: design by mechanochemistry. Advanced Energy Materials, 11(30), 2101022.
- X. Miao, H. Ni, H. Zhang, C. Wang, J. Fang, G. Yang, Li2ZrO<sub>3</sub>-coated 0.4Li<sub>2</sub>MnO <sub>3</sub>·0.6LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> for high performance cathode material in lithium-ion Power Storage, J. Power Sources 264 (2014) 147–154.
- 22. R.M. Salgado, F. Danzi, J.E. Oliveira, A. El-Azab, P.P. Camanho, M.H. Braga, The latest trends in electric vehicles batteries, Molecules 26 (2021) 3188.
- Helmers, L., Froböse, L., Friedrich, K., Steffens, M., Kern, D., Michalowski, P., & Kwade, A. (2021). Sustainable solvent-free production and resulting performance of polymer electrolyte-based all-solid-state Power Storage electrodes. Energy Technology, 9(3), 2000923.
- Lobato, B. (2021). Carbon Materials as Electrodes of Electrochemical Double-Layer Capacitors: Textural and Electrochemical Characterization. In Carbon Related Materials: Commemoration for Nobel Laureate Professor Suzuki Special Symposium at IUMRS-ICAM2017 (pp. 149-185). Springer Singapore.
- 25. Iro, Z. S., Subramani, C., & Dash, S. S. (2016). A brief review on electrode materials for supercapacitor. International Journal of Electrochemical Science, 11(12), 10628-10643.
- 26. Bhujun, B., Tan, M. T., & Shanmugam, A. S. (2017). Study of mixed ternary transition metal ferrites as potential electrodes for supercapacitor applications. Results in Physics, 7, 345-353.
- 27. Rao, S. S., Kanaka Durga, I., Naresh, B., Jin-Soo, B., Krishna, T. N. V., In-Ho, C., & Kim, H. J. (2018). One-pot hydrothermal synthesis of novel Cu-MnS with PVP cabbagelike nanostructures for high-performance supercapacitors. Energies, 11(6), 1590
- Thirumal, V., Pandurangan, A., Jayavel, R., Krishnamoorthi, S. R., & Ilangovan, R. (2016). Synthesis of nitrogen doped coiled double walled carbon nanotubes by chemical vapor deposition method for supercapacitor applications. Current Applied Physics, 16(8), 816-825
- 29. Fei, H., Saha, N., Kazantseva, N., Moucka, R., Cheng, Q., & Saha, P. (2017). A highly flexible supercapacitor based on MnO<sub>2</sub>/RGO nanosheets and bacterial cellulose-filled gel electrolyte. Materials, 10(11), 1251.
- Han, Y., Lei, Y., Ni, J., Zhang, Y., Geng, Z., Ming, P., & Xiao, Q. (2022). Single-crystalline cathodes for advanced Liion batteries: progress and challenges. Small, 18(43), 2107048
- 31. Wijareni, A. S., Widiyandari, H., Purwanto, A., Arif, A. F., & Mubarok, M. Z. (2022). Morphology and Particle Size of a Synthesized NMC 811 Cathode precursor with Mixed Hydroxide Precipitate and nickel sulfate as nickel sources and comparison of their electrochemical performances in an NMC 811 lithium-ion Power Storage. Energies, 15(16), 5794
- 32. Xiang, Y., Huang, M., Jiang, Y., Liu, S., Li, J., Wu, J., & Xiong, L. (2021). Ionic liquid assisted hydrothermal synthesis of 0.5Li<sub>2</sub>MnO<sub>3</sub>·0.5 LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> for lithium ion batteries. Journal of Alloys and Compounds, 864, 158177.

- 33. Jayachandran, M., Therese, H. A., & Vijayakumar, T. (2023). Tailored solution combustion method for enhancing high voltage electrochemical performance  $Li_{1.2}Ni_{0.1}Mn_{0.6}Co_{0.1}O_2$  as cathode material for lithium-ion batteries. Surfaces and Interfaces, 42, 103339
- 34. Dhere, S. (2018). Electrode materials for supercapacitors synthesized by sol–gel process. Current science, 115(3), 436-449.
- 35. Priyadharsini, C. I., Marimuthu, G., Pazhanivel, T., Anbarasan, P. M., Aroulmoji, V., Siva, V., & Mohana, L. (2020). Sol-Gel synthesis of Co 3 O 4 nanoparticles as an electrode material for supercapacitor applications. Journal of Sol-Gel Science and Technology, 96, 416-422
- Sun, M., Fang, Q., Li, Z., Cai, C., Li, H., Cao, B., & Fu, Y. (2021). Co-precipitation synthesis of CuCo<sub>2</sub>O<sub>4</sub> nanoparticles for supercapacitor electrodes with large specific capacity and high rate capability. Electrochimica Acta, 397, 139306
- Yadav, S., & Sharma, A. (2021). Importance and challenges of hydrothermal technique for synthesis of transition metal oxides and composites as supercapacitor electrode materials. Journal of Energy Storage, 44, 103295.
- Sisakyan, N., Chilingaryan, G., Manukyan, A., & Mukasyan, A. S. (2023). Combustion Synthesis of Materials for Application in Supercapacitors: A Review. Nanomaterials, 13(23), 3030
- Burmeister, C. F., & Kwade, A. (2013). Process engineering with planetary ball mills. Chemical Society Reviews, 42(18), 7660-7667.
- Gusev, V. G., Sobol'Kov, A. V., Aborkin, A. V., & Alymov, M. I. (2019). Simulation of the Energy–Force Parameters of Planetary Ball Mill Processing and Estimation of Their Influence on the Particle Size in an AMg2 Alloy/Graphite Composite Powder. Russian Metallurgy (Metally), 2019, 24-30
- Loh, Z. H., Samanta, A. K., & Heng, P. W. S. (2015). Overview of milling techniques for improving the solubility of poorly water-soluble drugs. Asian journal of pharmaceutical sciences, 10(4), 255-274
- Assadi, H., Kreye, H., Gärtner, F., & Klassen, T. J. A. M. (2016). Cold spraying–A materials perspective. Acta Materialia, 116, 382-407.
- Moridi, A., Hassani-Gangaraj, S. M., Guagliano, M., & Dao, M. (2014). Cold spray coating: review of material systems and future perspectives. Surface Engineering, 30(6), 369-395
- Wang, X., Feng, F., Klecka, M. A., Mordasky, M. D., Garofano, J. K., El-Wardany, T.,& Champagne, V. K. (2015). Characterization and modeling of the bonding process in cold spray additive manufacturing. Additive Manufacturing, 8, 149-162
- Champagne Jr, V. K., Ozdemir, O. C., & Nardi, A. (Eds.). (2021). Practical cold spray. Cham, Switzerland: Springer International Publishing
- Wang, X., Feng, F., Klecka, M. A., Mordasky, M. D., Garofano, J. K., El-Wardany, T.,& Champagne, V. K. (2015). Characterization and modeling of the bonding process in cold spray additive manufacturing. Additive Manufacturing, 8, 149-162
- 47. Dykhuizen, R. C., & Smith, M. F. (1998). Gas dynamic principles of cold spray. Journal of Thermal spray technology, 7, 205-212.
- Assadi, H., Gärtner, F., Stoltenhoff, T., & Kreye, H. (2003). Bonding mechanism in cold gas spraying. Acta materialia, 51(15), 4379-4394.
- Yaseen, M., Khattak, M. A. K., Humayun, M., Usman, M., Shah, S. S., Bibi, S.,& Ullah, H. (2021). A review of supercapacitors: materials design, modification, and applications. Energies, 14(22), 7779.
- 50. Li, W., Erickson, E. M., & Manthiram, A. (2020). High-

nickel layered oxide cathodes for lithium-based automotive batteries. Nature Energy, 5(1), 26-34.

- 51. Wang, X., Yasukawa, E., & Kasuya, S. (2001). Nonflammable trimethyl phosphate solvent-containing electrolytes for lithium-ion batteries: I. Fundamental properties. Journal of The Electrochemical Society, 148(10), A1058.
- 52. Stein IV, M., Chen, C. F., Mullings, M., Jaime, D., Zaleski, A., Mukherjee, P. P., & Rhodes, C. P. (2016). Probing the effect of high energy ball milling on the structure and properties of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> cathodes for Li-ion batteries. Journal of electrochemical energy conversion and storage, 13(3), 031001.
- Li, Q., Dang, R., Chen, M., Lee, Y., Hu, Z., & Xiao, X. (2018). Synthesis method for long cycle life lithium-ion cathode material: Nickel-rich core-shell LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>.ACS applied materials & interfaces, 10(21), 17850-17860.
- 54. Widiyandari, H., Latifah, R. A., Jumari, A., Yudha, C. S., & Nisa, S. S. Sintesis Material Katoda LiNi<sub>0,8</sub>Mn<sub>0,1</sub>Co<sub>0,1</sub>O<sub>2</sub> (NMC811) dengan Metode Solid State Menggunakan Nikel Hasil Perolehan Kembali dari Spent Nickel Catalyst. ALCHEMY Jurnal Penelitian Kimia, 18(2), 214-220.
- 55. Pan, T., Alvarado, J., Zhu, J., Yue, Y., Xin, H. L., Nordlund, D.,& Doeff, M. M. (2019). Structural degradation of layered cathode materials in lithium-ion batteries induced by ball milling. Journal of the electrochemical society, 166(10), A1964.
- 56. Zybert, M., Ronduda, H., Dąbrowska, K., Ostrowski, A., Sobczak, K., Moszyński, D., ... & Wieczorek, W. (2022). Suppressing Ni/Li disordering in LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode material for Li-ion batteries by rare earth element doping. Energy Reports, 8, 3995-4005.
- Ding, Y., Zhang, P., Jiang, Y., & Gao, D. (2007). Effect of rare earth elements doping on structure and electrochemical properties of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> for lithium-ion battery. Solid State Ionics, 178(13-14), 967-971.
- Dong, M. X., Li, X. Q., Wang, Z. X., Li, X. H., Guo, H. J., & Huang, Z. J. (2017). Enhanced cycling stability of La modified LiNi<sub>0.8x</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>La<sub>x</sub>O<sub>2</sub> for Li-ion battery. Transactions of Nonferrous Metals Society of China, 27(5), 1134-1142.
- 59. Jia, X., Yan, M., Zhou, Z., Chen, X., Yao, C., Chen, D., & Chen, Y. (2017). Nd-doped LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> as a cathode material for better rate capability in high voltage cycling of Li-ion batteries. Electrochimica Acta, 254, 50-58.
- Zeng, Y., Qiu, K., Yang, Z., Zhou, F., Xia, L., & Bu, Y. (2016). Influence of europium doping on the electrochemical performance of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cathode materials for lithium-ion batteries. Ceramics International, 42(8), 10433-10438.
- Shi, Y., Kim, K., Xing, Y., Millonig, A., Kim, B., Wang, L., & Wen, J. (2020). Facile and scalable dry surface doping technique to enhance the electrochemical performance of LiNi<sub>0.64</sub>Mn<sub>0.2</sub>Co<sub>0.16</sub>O<sub>2</sub> cathode materials. Journal of Materials Chemistry A, 8(38), 19866-19872.