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Research Article

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Recent progress in nanomaterials of battery energy storage: A patent landscape analysis, technology updates, and future prospects

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Abstract: The world's energy demand has significantly increased as a result of the growing population and accompanying rise in energy usage. Fortunately, the innovation of nanomaterials (NMs) and their corresponding processing into devices and electrodes could enhance the functionality and/or advancement of the current battery energy storage systems (BESSs). Patent landscape analysis (PLA) can offer a comprehensive overview of technological development trends and enable discussion in interdisciplinary areas that facilitate more rational technology planning in the future. In this study, PLA of recent advancements in the NM-based BESS was critically analyzed, future technologies forecasted, and potential challenges outlined. A search was performed in the Lens database using "energy storage system," "battery," and "nanomaterial," and related patents under the simple family were extracted. Finally, after excluding duplicates and irrelevant patents, a total of 89 patents were selected for analysis using various parameters. The article provides a current technical overview along with an extensive bibliographic review of the patent family, trends of patent growth, key inventors and owners, patent legal status, patent jurisdiction, top cited patents, *etc*., as well as technological updates. Overall, nanotechnology has great potential for the future; however, further research and studies are necessary to accelerate the widespread usage of NMs in energy storage systems using cost-effective and environmentally friendly technologies.

Keywords: nanomaterials, patent landscape analysis, battery energy storage, nanostructured materials, technology updates

1 Introduction

The primary power source for most energy use is moving quickly and dramatically toward electricity. The demand for portable consumer devices, medical devices, electric vehicles, and electric grids, as well as the growing Internet of Things and wearable devices, has made reversible electricity storage and release an important technology. These uses, the requirement to store power energy generated by piezoelectric and triboelectric generators, wind turbines, heat sources, solar panels, and moving machinery all necessitate significant advancements in and diversification of the technology of energy storage [1,2]. New, inexpensive, and environmentally acceptable energy conversion and storage devices must now be developed in order to meet the demands of contemporary society and growing ecological concerns; this is the reason for the field's fast advancement of research. The features of the materials used in these devices have a significant impact on their operational efficiency. The key to the advancements in energy conversion and storage that have already been accomplished is the chemistry of innovative materials. In this instance, materials with large electrochemically active surfaces and nanometer-sized structural characteristics can shift the usual approach for energy storage [3]. Numerous forms of research and studies have been focused on the creation of ideal energy storage systems (ESSs) worldwide as a result of the rising demand for attractive ESSs. Energy storage and conversion technologies, including batteries, supercapacitors, and solar cells, have undergone substantial development in response to the looming depletion of traditional fossil fuels and the

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growing challenge posed by the carbon dioxide footprint. These erratic and intermittent sources must be seamlessly incorporated into the power grid system, which calls for an experienced, substantial, and reasonably priced ESS. Due to their special characteristics, such as high energy density, long life, availability, low cost, and high safety, batteries have received a lot of interest from academics, scientists, and researchers throughout the world [4]. Conte [5] presented an overview of the performance of the various electro-static discharges (ESDs) (Table 1). It is obvious that lithium-ion batteries (LIBs) have higher power and energy densities than other energy storage technologies. It also has certain appealing characteristics including high efficiency, a long life cycle, a low discharge rate, and a high voltage.

Nanomaterials (NMs) have characteristics that allow them excellent candidates for a variety of energy storage technologies. NMs can differ greatly from one another in their properties, giving researchers countless opportunities to enhance devices for energy storage. The superior electrical conductivity and charge carrier mobility of certain NMs, which allow electrons to move and be stored effectively, is one of the key advantages of ESDs [6]. Due to the remarkable mechanical, electrical, and optical features conferred by restricting the dimensions of such materials, as well as the contribution of both bulk and surface attributes to overall behavior, nanostructured materials have gained considerable interest in recent years. To understand the possibilities of smaller-scale materials, one needs to look at the incredible advances in microelectronics. Materials with nanostructures are becoming more and more crucial for electrochemical energy storage [3,7].

Due to their large specific surface area and excellent electrical, physicochemical, and mechanical properties, NMs have received a lot of attention for energy storage. A wide range of innovative nanostructured materials and composites with customized morphologies have arisen thanks to cutting-edge nanofabrication processes, and they have been investigated as electrodes for supercapacitors and/or LIB and Na-ion battery applications [8]. In comparison to most other shapes of substances, the structures of NMs, particularly their length, large surface area, and high porosity, offer distinct advantages, and their versatility in that they may be adapted to particular needs and increase their utilization. The employment of NMs as an anode and cathode will increase surface reactivity and, consequently, the effectiveness of energy products due to their vast surface area [9]. Therefore, current progress in ESDs is due to the manufacturing of nanostructured electroactive materials on a large scale.

A patent is a document that comprises technical information that was created through scientific invention by its creators and is registered with the appropriate international agencies to safeguard its intellectual property rights [4]. Patents are the rights to intellectual property that can be given in exchange for the disclosure of an invention and are used to protect inventions within the borders of specific jurisdictions. A granted patent has commercial significance since it grants the exclusive right to prevent anyone from producing, using, or selling the invention in the designated territory. A patent's capacity to keep competitors out of a market or from using a protected technology has led to the term "limited monopoly" being applied to it. Understanding which companies own patents and what technology fields they cover can have a big impact on legislation and corporate decision-making because of the potential commercial and legal implications. In addition, patents are not available everywhere else; hence, it is considered critical sources of innovation [10]. The application of patent data and the analysis of this data is essential to the management of technology. Usually, the analysis of the technology revealed in patents and the identification of the legal status and specific features of patents provide an important tool that may be properly understood [4].

A popular technique for analyzing current trends in research, developments, and patenting patterns, as well as

Table 1: An overview of the performance of the various ESDs

Battery types	Temperature (°C)	η (%)	Energy		Power (W/kg)	Voltage (V)	Self-discharge (%/month)	Cycle life at 80%DOD	Cost estimation	
			(W h/l)	(Wh/kg)					($/kW h)	($/kW)
Lead acid	−30 to 60	85	50–70	20–40	300	2.1	4–8	200	150	10
Nickel metal hydride	−20 to 50	80	200	40–60	1,300–500	1.2	20	>2,500	500	20
Li-ion	−20 to 55	93	150–200	100–200	3,000–800	~3.6	1–5	<2,500	800	50–75
Electric double-layer capacitor	−30 to 65	97	5	5–20	1,500	~2.5	30	Not applicable	2,000	50

Reproduced with permission from Conte [5].

the regulations pertaining to the current technology, is the patent landscape (PL) review. Inventors and researchers can use patent landscape analysis (PLA) to gain important technological insights that will help them create fresh solutions to real-world problems [11]. In addition to assisting in the understanding of current technology developments, patent landscaping serves as a tool in locating key industry players that potential rivals may encounter. These studies may also be used to license or purchase prospects for businesses with patents on their names. PLs identify areas for future growth and provide data that enable decisions to be made with knowledge and based on evidence. The main advantage of a PLA is an in-depth understanding of the product, technology, and competition in the chosen geographic region for the search [12].

A tried-and-true multistep process known as PLA-often defined as "patent mapping" – uses both human intelligence and computer tools to filter through, compile, and extract value from this vast amount of data. In summary, PLA clarifies the discoveries that serve as the foundation for goods and technologies. A complete PL analysis project consists of a set of technological references and accompanying analytics from which important legal, technical, and commercial data can be obtained. Large organizations, research centers, universities, investors, and startups may comprehend and make informed decisions before investing time and money in new innovation and product development alternatives [13]. Researchers and decision-makers from a variety of disciplines are interested in statistical analyses based on patent data because patents can act as quantitative indicators of phenomena that are challenging to evaluate such as knowledge spillovers, innovation, collaboration, and technical space [14]. Therefore, institutions, companies, and organizations could benefit significantly from the analysis of patent documents.

There are numerous internet databases available to simplify and facilitate PLA such as the United States Patent Office, the European Patent Office, the United States Food and Drug Administration (Orange Book), Google Scholar, the Lens database, ClinicalTrials.gov, *etc.* [15]. Among these databases, Lens currently attracts more attention from researchers due to its abundant facilities. With the addition of OpenAlex and UnPaywall open-access information linkages and more than 200 million academic records collated and managed by Microsoft Academic, PubMed, and Crossref, Lens offers a wealth of information. For the first time, the entire Scholarly Citation Map is accessible as a free public resource. To locate the most pertinent and significant patents, the Lens patent search feature provides advanced Boolean operations, structured search, biological search, taxonomy search, filtering, and sorting choices. Make shareable collections, notes, and visualizations that may be annotated (see https://www.lens.org/lens/). To create an open map of the world of knowledge-directed innovation, the Lens will enable the sharing, aggregation, and embedding of document collections, aggregates, and analyses. In the end, this will reinstate the patent system's function as a learning tool to educate and motivate businesspeople, citizens, and decision-makers [16].

Until now, numerous PLA reviews have been reported for various fields of research. However, no PLA review has been introduced related to technological advances in NM-based battery energy storage systems (BESSs). However, demands for the NM-based BESS are increasing day by day. According to Stratview Research, the global market for ESS is anticipated to reach 440.71 GW in 2028, expanding at a common annual growth rate of 11.1% from 2022 to 2028. The present study aims to summarize the historical development of scientific literature and the PL beyond the invention of NM-based BESS in order to provide an overview of current advancements in basic and applied research using the Lens database. To the best of our knowledge, this study is the first analysis of the NM-based BESS PL. Herein, an overview of patents and scientific articles is provided, incorporating the advancement of scientific knowledge with the PL for NM-based BESS. In general, reviewing the technology revealed in patents and determining its legal status and features yield a useful tool that can be easily comprehended. Therefore, the following contributions, objectives, and novelty are achieved by this article:

- Conducting a comprehensive search and retrieval of relevant patents related to an NM-based BESS.
- The identification of markets that are safeguarded by competitors within the realm of technology.
- This study provides an overview of innovation in a specific technical field at any given period. It may also depict the trajectory of technologies, key players (top international companies), and locations of innovation.
- Scientists and researchers acquire crucial information and recent awareness about a certain technology in order to develop, modify, or improve it.
- It provides an obvious depiction of how the novel idea would function in practice.
- Teams of business developers identify the significant assignees (owners) of the pertinent technology, which is useful information to take into account when considering potential merger and acquisition partners, in- and out-licensing prospects, clients, or suppliers, as well as when determining whether it would be more profitable to develop the technology.
- A great forum of thoughts to exchange ideas on important commercial challenges is provided by PLA. A comprehensive and unified internal business process that

spans the entire organization is stimulated by PLA, which also improves communications between departments.
- This analysis supports academic institutions, large corporations, new ventures, and the like in making the right decisions prior to investing time and resources in the development of an innovative concept in the field.

2 NM-based energy storage technology updates

Nowadays, the consumption of energy in all its forms is unavoidable and increasing. Fossil fuels currently make up the majority of energy sources. The growth of renewable energy sources has, however, gained much attention due to the serious condition of global warming. The employment of nanoparticles as an anode and cathode will increase surface activity and, consequently, the efficiency of energy products due to the huge surface area. Already, advances in nanotechnology are enhancing the conversion, storage, and transfer of energy. Future developments in the energy sector may heavily rely on nanotechnology solutions, particularly when it comes to the creation of novel methods for energy storage [17]. Through innovative technological solutions and improved manufacturing technologies, nanotechnologies play a significant role in improving energy effectiveness in every sector of the industry and boosting the economic viability of renewable energy generation. Innovations in nanotechnology may have an impact on all sectors in the value-added chain of the energy field.

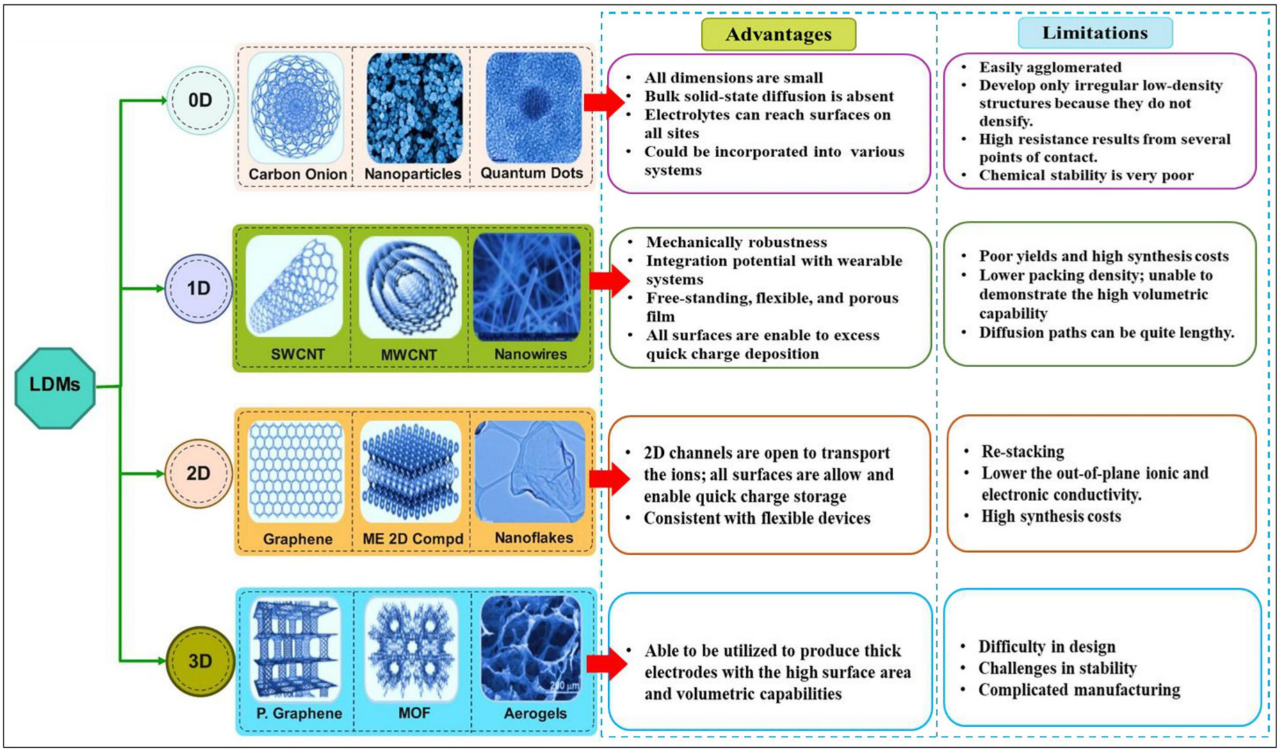
2.1 Energy conversion

Nanotechnology can improve how effectively and sustainably basic energy sources, such as the sun, are converted into electrical, thermal, and kinetic energy. Currently, new techniques such as size/facet control, atomic regulation, vacancy engineering, structural engineering, and the creation of nanocomposites change the active sites' physicochemical characteristics (*e.g.*, optical, electronic, textural, and band properties). Consequently, this leads to a significant increase in the ability of NMs to convert and store energy [18]. Nanostructured materials and nanotechnology are making significant contributions to the field of solar photovoltaics, or solar cells, which convert sunlight into electricity. A successful study could lead to a significant decrease in the cost of making these solar cells while simultaneously increasing efficiency.

It has been proposed to use colloidal quantum materials made of nanoparticles based on semiconductors as photocatalysts to convert solar energy into chemical work. Water splitting is one of the primary photocatalytic processes that has been studied. It tries to use the energy absorbed by nanocrystals to directly produce hydrogen gas and oxygen by reducing and oxidizing water, respectively. The hydrogen gas can then be managed to react with oxygen to create backwater in a fuel cell, producing power and creating a cycle with no emissions. Being able to tune and tailor the electronic band structure of the nanoparticles by composition, shape, and size, the high surface-to-volume ratio and the capability to use tiny particles either directly in solution or incorporated into a matrix have all led to the investigation of various systems for water splitting, primarily by separation of the two half-cell reactions. Furthermore, because of their properties' adaptability, systematic investigations might be carried out to identify the key variables that control their performances and understand their mode of operation [19].

Nanostructured materials that are less than 100 nm in at least one dimension are referred to as low-dimensional materials (LDMs). Metals, insulators, and semiconductors are examples of LDMs. The LDMs can be categorized into various groups based on their morphologies such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) [20–22]. LDMs have exceptional chemical, electrical, mechanical, and optical characteristics that result from the quantum confinement effect, and their large surface area-to-volume ratio greatly enhances the opportunity to be used in energy conversion and storage. Comparable to their bulk counterparts, low-dimensional semiconductor materials have distinctive optical and electrical characteristics. A brief discussion of LDMs is given below, and relevant diagrams are illustrated in Figure 1. The quantum confinement effect describes how the nanostructures of LDMs constrain the motion of electrons. Low-dimensional NMs have special features as a result of quantum confinement, which might improve the efficiency of photocatalysts [23]. Due to their extremely small size (usually 1.2–10 nm), quantum dots (QDs), which exhibit distinctive optical and electrical properties, are 0D nanostructures in which the transport of electrons is spatially constrained in three dimensions. Numerous QD photocatalysts have been shown to work with a variety of materials, including graphene [24], ZnSe [25], CdS [26], $CuInS_2$ [27], NiS_2 [28], PbS [29], *etc.*, all of which exhibit these advantageous features as well as excellent candidates for effective CO_2 conversion.

Materials with a 1D structure have 2D confinement to the electron's mobility. For 1D NMs, nanowires (NWs),



Advantages

0D:
- All dimensions are small
- Bulk solid-state diffusion is absent
- Electrolytes can reach surfaces on all sites
- Could be incorporated into various systems

1D:
- Mechanically robustness
- Integration potential with wearable systems
- Free-standing, flexible, and porous film
- All surfaces are enable to excess quick charge deposition

2D:
- 2D channels are open to transport the ions; all surfaces are allow and enable quick charge storage
- Consistent with flexible devices

3D:
- Able to be utilized to produce thick electrodes with the high surface area and volumetric capabilities

Limitations

0D:
- Easily agglomerated
- Develop only irregular low-density structures because they do not densify.
- High resistance results from several points of contact.
- Chemical stability is very poor

1D:
- Poor yields and high synthesis costs
- Lower packing density; unable to demonstrate the high volumetric capability
- Diffusion paths can be quite lengthy.

2D:
- Re-stacking
- Lower the out-of-plane ionic and electronic conductivity.
- High synthesis costs

3D:
- Difficulty in design
- Challenges in stability
- Complicated manufacturing

Figure 1: Overview of different types of LDMs based on their morphology: 0D, 1D, 2D, and 3D NMs. An illustration of the chemical, structural, and morphological features, advantages, and limitations of the LDMs that can be used for ESDs with improved performance. Reproduced with permission from Pomerantseva *et al.* [1].

nanotubes, and nanorods are typical morphologies. The 1D structure gives materials exceptional charge transport and longer carrier lifetimes because of the special state density distribution and innately higher reactivity resulting from a larger surface area compared to bulk materials [30–32]. Numerous semiconductor materials have been created with a 1D structure to take advantage of these intriguing properties, and these nanostructures have drawn a lot of interest in increasing the photocatalytic conversion of CO_2 into solar fuels [33]. Due to its low cost, nontoxicity, and chemical stability, TiO_2 is one of the photocatalytic materials for CO_2 conversion that has been studied the most [30]. Another material with promise for photocatalytic CO_2 conversion is graphitic carbon nitride (g-C_3N_4). A polymeric semiconductor photocatalyst without metals is called g-C_3N_4. Due to its excellent photocatalytic efficiency, g-C_3N_4 has attracted a lot of attention in photocatalysis research. The photocatalytic activity of g-C_3N_4 has been greatly enhanced by means of nanostructuralization, elemental doping, surface modification, and hybridization [34,35]. 2D NMs have promising applications for developing ESSs having high power density and volumetric energy [36]. Nanosheets (NSs) are 2D materials with flake-shaped morphologies and thicknesses ranging from a few atoms to about 100 nm [37]. Due to their large surface area, excellent ion transport efficiency, and abundance of easily accessible active sites, 2D materials are highly suitable for ESDs [38,39]. Because of the quantum confinement phenomenon, 2D materials exhibit different electrical and optical characteristics from bulk materials. However, when these materials are thinned to extremely thin NSs (monolayers), the optical and electrical properties of NS are further enhanced [33]. In addition, graphene possesses a range of exceptional properties due to its distinctive 2D planar structure. These properties include the half-integer quantum Hall effect, ultrahigh carrier mobility as predicted by theoretical calculations and observed in electronic devices, high thermal conductivity, large specific surface area, and the utmost durability [40]. Due to its great charge carrier mobility, graphene, the most prevalent 2D material, has been researched in a variety of domains, including photocatalysis [41]. Materials composed of 2D NSs exhibit several distinctive characteristics that make them highly desirable for future energy storage devices. These properties include an ultrathin thickness and a substantial lateral size, resulting in a layered structure. Additionally, these materials possess an abundance of catalytically active sites that are easily accessible. Furthermore, they exhibit unconventional physical, chemical, and electronic properties, further enhancing their appeal as potential candidates for next-generation energy storage [42]. Researchers demonstrated numerous 2D materials to produce solar fuels including boron-nitride (BN) [43], bismuth-based materials [44,45], WS_2 [46], MoS_2 [47], *etc.* There are some challenges to overcome for 2D transition metal oxides and hydroxides, such as the few types of 2D parent materials that are available in bulk, the controlled synthesis of 2D nanostructures with unlayered structures, and the capacity to regulate the characteristics of layers by adjusting the chemistry and nanoscopic features [48].

Recently, in the production of electrodes for high-performing electrochemical ESSs, 3D structures have received greater interest. In contrast to other types of LDMs, 3D materials have the ability to speed up electron transportation by reducing conductive pathways. In addition, 3D materials improve the performance of the devices because their porous composite structure and large surface area create large contact areas with the electrolyte and continuous paths for ions to move through the whole area [49]. It is essential to create 3D architecture that is optimized for both electron and ion transport in order to create thicker electrodes (*e.g.*, 100–200 mm) with high area and volumetric storage properties. These architectural designs would reduce the number of passive components such as current collectors and separators, which take up extra space and dead weight-in cells [1]. In order to assure incredibly efficient charge distribution to and from the electrodes, 3D architectural material provides interpenetrating transport channels for ions and electrons. To convert the remarkable performance of 3D materials into macroelectrodes with significant mass loading, several transport pathways are required [50]. Furthermore, the 3D graphene networks exhibit a significantly porous structure, hence enhancing the rate of reaction kinetics and resulting in elevated energy and power density [51]. Until now, numerous 3D materials have been developed to enhance the performance of ESSs [50,52–54]. However, fabricating 3D architecture material-based energy storage system devices in an efficient and cost-effective manner is still challenging. To fabricate dense and high-mass-load electrodes with convenient 3D structures, new techniques and methods need to be developed. Among fabrication techniques, holographic patterning and 3D printing are considered rapid, inexpensive, and scalable methods for manufacturing. Another method involves using biological materials as templates to create ultra-thick electrodes having 3D hierarchical structures [50,55]. Due to their considerable energy capacity and lower toxicity, 3D transition-metal oxides, particularly Fe_3O_4, have received a lot of interest recently as anode materials. For example, Yang *et al.* [56] synthesized 3D nanostructured and hollow sphere Fe_3O_4/C composites using porous spongy carbon and $FeCl_3·6H_2O$ raw materials and a facile solvothermal method. The composite showed remarkable electrochemical properties that achieved relatively large reversible specific capacity, strong cycle stability, and significant rate capability. A brief discussion is given below, and relevant diagrams are illustrated in Figure 1.

2.2 Energy storage

Batteries and supercapacitors in particular can benefit greatly from the use of nanotechnology in ESSs. When not linked to the electricity grid, such as when a mobile phone is being used, batteries are required to supply electrical energy. Nanotechnology can be used to develop materials to create heat-resistant, flexible, and high-performance electrodes for LIBs. Nano-porous materials like zeolites, which might be employed as heat stores in both residential and commercial grids, could also be better utilized for thermal energy storage. Nanotechnologies have the potential to significantly increase the capacity and security of LIBs, as demonstrated by innovative ceramic, heat-resistant, and stiff-flexible separators and high-performance electrode materials, for example [57].

Another significant advancement in energy research is the use of nanotechnology to improve ESSs. For example, nickel-cobalt metal-organic framework (NiCo-MOF) NSs with several layers were developed by Chi *et al.* [58] as durable electrode materials for enhanced electrochemical energy storage over 3,000 cycles at $5\,A\,g^{-1}$. In a silicon oxycarbide (SiOC) matrix, Dubey *et al.* [59] reported a generation of homogeneously implanted Sb nanoparticles that were able to offer a very large Li-ion storage capacity. For improved charge storage capacity and rate performance for LIBs, Gu *et al.* [60] developed the intercalative hybridization of MoS_2 with chromium hydroxide nanoclusters, which stabilizes the open porous stacking structure, speeds up charge kinetics and basal spacing. In addition, the separator was built by Jiang *et al.* [61] using a thin porous carbon NS with embedded TiO_2 nanoparticles as an interlayer, which promotes faster Li-ion diffusion while concurrently inhibiting polysulfide diffusion.

Carbon is considered an excellent energy storage material due to its unique properties, including its high availability, lower specific weight, and high electronic conductivity. Furthermore, a variety of carbon structures and morphologies are easily obtainable as a result of $sp/sp_2/sp_3$ hybridization. However, nanostructured carbons often offer little redox potential, generally exhibiting redox capacity after being functionalized. Consequently, instead of being used as the active material for ESDs, they are typically used as a conducting support backbone or as a material for double-layer capacitors [62,63]. Conversely, graphite, which is made up of layers of ordered graphene, shows exceptional properties; it has a capacity of 372 mA h g^{-1} for storing Li ions in the spaces between the layers [64].

2.2.1 NMs for anodes

The theoretical capacity (TC) of Si is much higher than that of other NMs; for example, its TC is ten times higher than that of graphite (372 mA h g^{-1}). Consequently, Si is a widely used and favorite anode material for the ESSs of future generations. This higher capacity of Si NMs is due to their alloying mechanism, which enables single Si to host up to 4.4 Li ions. Moreover, Si NMs are capable of providing poor cyclability because of their ability to expand the volume significantly (>300%) during lithiation [65–67]. The tension caused by the volume change causes the electrode to crack and possibly get pulverized, which results in a loss of electrical contact and fast capacity fading. Furthermore, the solid–electrolyte interphase (SEI) can be disrupted by continual expansion and contraction during cycling, which leads to lower Coulombic efficiency (CE) because of repetitive SEI production [68,69]. The Si anode serves as an excellent example of how nanotechnology can be used to solve material problems in battery development. The pulverization problem was solved by decreasing the Si material size down to the nanoscale. According to previous reports, Si is able to contract and expand except in pulverization at sizes less than 300 nm, termed as the crucial fracture size [70]. For instance, Guo *et al.* [71] used the thermal burst method for synthesizing Si nanotube sheets. The Si nanotube sheets exhibit a discharge specific capacity of 712.7 mA h g^{-1} at a current density of 5 A g^{-1}. More recently, arrays of Si micropillars were developed by employing photolithographic patterning and optimized deep reactive ion etching procedure utilizing a Si wafer. The Si micropillar electrode (length of 14 μm) exhibited a notable specific capacity of 2,600 mA h g^{-1} and a significant areal capacity of 3 mA h cm^{-2}, which remained stable for more than 100 cycles [72]. For instance, Si NWs grown directly on the current collector using a vapor, liquid, and solid approach were used in the first-generation Si anode that our group reported at the end of 2007, and a noticeable improvement in electrochemical performance was found compared with thick films and big particles. However, there are a few challenges for using silicon anodes, including (i) destabilization of the SEI and structural degradation due to the significant volume change (~300%) that occurs during cyclin, (ii) incidence of electrolytic side reactions, and (iii) with the poor volumetric capacity that results from the material's reduction in size to the nanometer scale [73–76].

To overcome these challenges, Batool *et al.* [77] fabricated nanostructured composites consisting of a silicon core and a carbon shell (Si@C) consisting of a thin and homogeneous porous carbon layer at the interface (Figure 2a and b). The utilization of mesoporous conductive carbon efficiently regulated the mechanical strain of silicon NPs, hence preserving the structural integrity of Si@C nanocomposites. Additionally, it facilitated easy access to electrolytes and facilitated the efficient transport of short Li ions. The innovative Si@C anode demonstrated a consistent specific capacity of around 868 mA h g^{-1} at a current rate of 0.1 A g^{-1} for up to 500 cycles, with a columbic efficiency of 99%. Similarly, Ding *et al.* [78] effectively synthesized the SiO_2@a–TiO_2@Ag composite with a core–shell structure using a simple sol–gel technique. The composite plays a role in mitigating the expansion of the electrode and offers additional pathways for Li-ion diffusion due to the elastic behavior of the TiO_2 layer. Furthermore, Ag NPs have excellent electrical conductivity.

Conversely, due to its largest TC (3,860 mA h g^{-1}) and lowest electrochemical potential (3.04 V *vs* the conventional hydrogen electrode), Li metal is the ideal anode. The significant interfacial variation, which internally impairs the delicate SEI layer, promotes a dendritic Li deposition that may result in an internal short circuit and damage battery safety. The repetitive Li plating/stripping (deposition/dissolution) operations produce a lot of Li dendrites on the anode surface and have a lower CE, according to previous studies [79]. Furthermore, the recurrent SEI breakdown/repair and high-surface-area dendrites drastically reduce the cycle life. Li metal research has recently seen a resurgence thanks to the advancement of nanotechnology, and the results of this study have been well-reviewed in various reviews [79–82]. They were aiming to determine characterization techniques suited for *in situ* observation and study of SEI development to gain insight into the electrochemical processes occurring in the cell while eliminating the parameters that favor the generation of this type of surface structures.

In order to get over the aforementioned issues, the main objective is to provide homogenous Li deposition throughout Li plating and stripping, protecting Li metal against dendrite growth. To date, numerous approaches have been put forth to produce high-performance Li metal anodes. Figure 3 summarizes the process and related method or rationale for enhancing the Li metal anodes' long-term cycle stability using an ionically conductive coating that is thick, thin, and protective (either before or during cycling) (Figure 3a). A protective layer or matrix

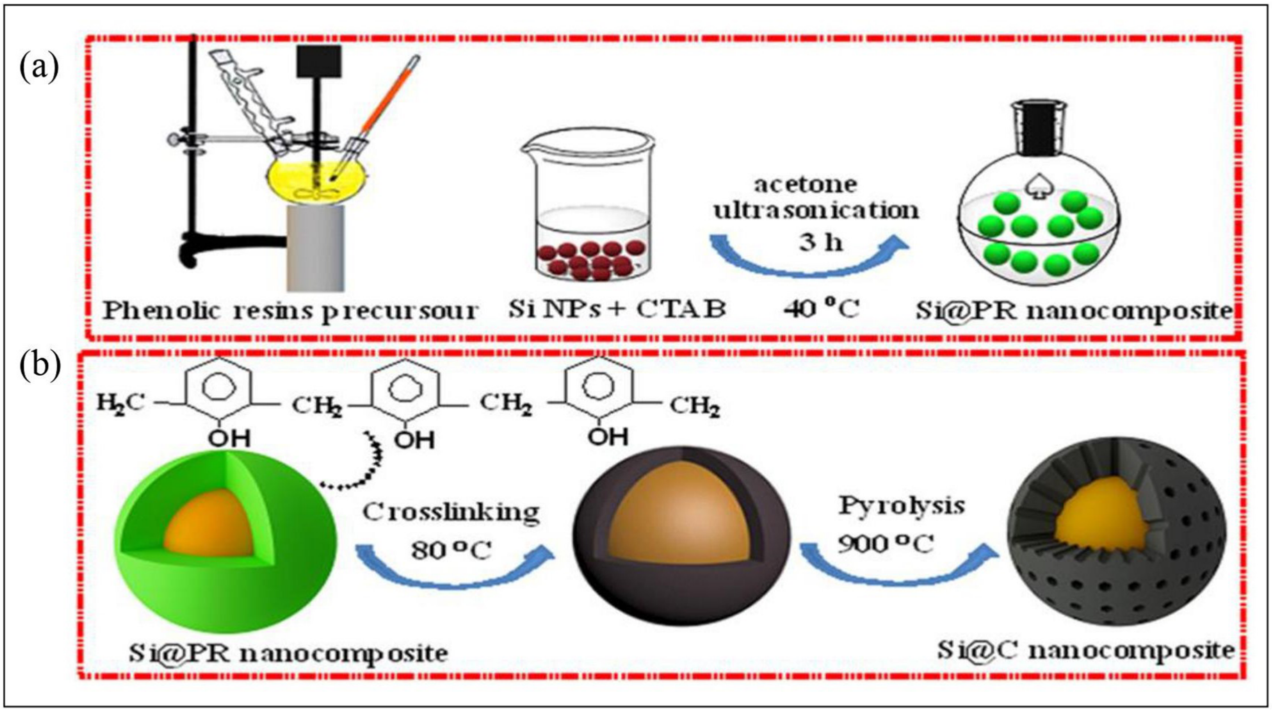


Figure 2: (a) A schematic mechanism for the fabrication of phenolic resins-based interfacial coating on commercial silicon nanoparticles through ultrasonication and (b) further pyrolysis for anode material preparation and application in LIBs. Reproduced with permission from Batool *et al.* [77].

for the electron conductor was also used on the Li metal anode in addition to the ion conductor (Figure 3b). In order to further enhance the stability of the reaction contact and prevent the formation of Li dendrites, much effort was made into designing lithiophilic hosts with complex topologies containing active Li (Figure 3c). Moreover, electrolyte modifications (Figure 3d), various binder designs (Figure 3e), and modified separators are more effective for preventing Li dendrite penetration (Figure 3f) [79].

A brief description of the process and related method for enhancing the long-term cycle stability of Li metal anodes is given as follows:

a) *Ionic conductor:* Movement of ions from one place to another according to an ionic gradient. This phenomenon is described in elementary science as a characteristic of liquid electrolyte solutions. Example: Type I and type II batteries, fuel cells, electrochromic windows and displays, solid-state sensors, *etc*.
b) *Electron conductor:* Movement of electrons or charge from one place to another in response to an electric field such as metals and semiconductors.
c) *Lithium host:* Lithium (Li) hosts, which may electrochemically deposit Li in existing pores of 3D frameworks, have been studied as a sophisticated electrode structure for Li-metal batteries with high energy density. The Li metal anode undergoes a substantial change in volume throughout the plating/stripping process, leading to the fracturing of the SEI, the production of dendrites, the depletion of electrolytes, and a low CE. By employing a suitable Li host matrix that possesses consistent Li nucleation sites, it is possible to reduce the significant change in the volume of Li metal and achieve uniform regulation of Li dendrites throughout the cycling process [79].
d) *Electrolyte modification:* Upon contact between the metal anode and the nonaqueous electrolytes, it was discovered that a thin film of intricate composition was spontaneously generated. The electrolyte composition has a crucial role in the creation of the SEI, which is thin, stable, dense, and elastic. Hence, altering the composition of electrolytes, such as solvents, salts, and additives, has been considered the most efficient approach to enhance the stability of Li metal anodes. There are several methods for modifying electrolytes, such as ion doping and substitution, coating, composite method, *etc.* [79].
e) *Binder design:* Binder designs have been utilized as successful approaches to reduce volume changes and inhibit the growth of Li dendrites in LIBs. Applying an appropriate binder can effectively mitigate the formation of cracks in Li metal anodes throughout the cycling process, leading to the establishment of a consistent and stable interphase [79]. For example, a binder made of poly

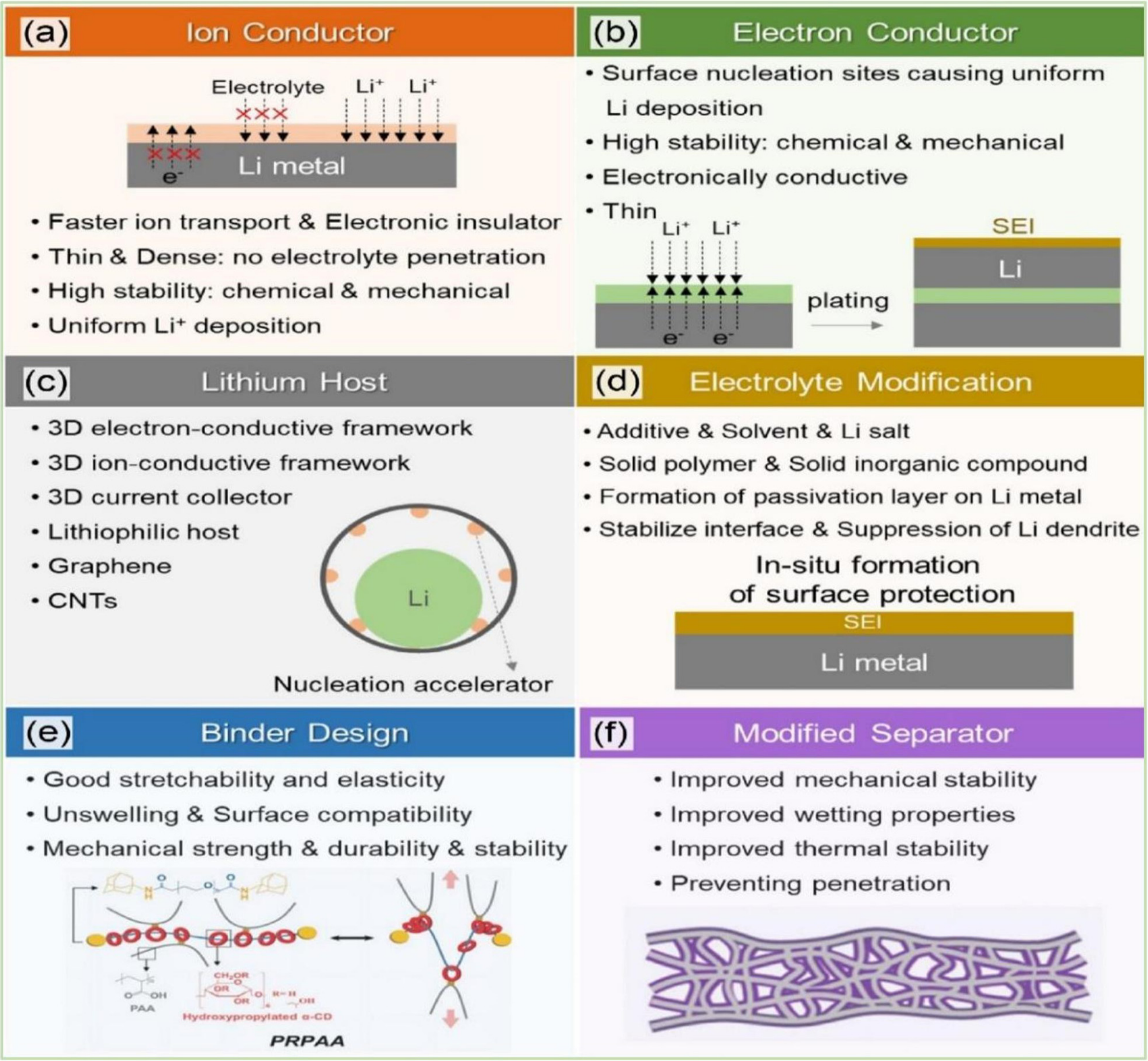


Figure 3: By preventing lithium metal from the formation of Li dendrites during Li plating and stripping, a uniform Li deposition may be achieved, which will help overcome challenges. Principal methods for enhancing high-performance Li metal anodes and their justification: formation of (a) ion conductor layer and (b) electron conductor layer on Li metal anode, (c) design of Li hosts, (d) modification of electrolyte, (e) binder design, and (f) modification of separator. Reproduced with permission from Wang *et al.* [79].

(acrylic acid) incorporated with polyrotaxane is used to enhance the mechanical integrity of the electrode in an Li metal anode. This binder is able to tolerate the large stress caused by repeated Li uptake and release, preventing the formation of cracks during operation [83].

f) Modified separator: Modifications to separators have been used as effective solutions to address volume change and inhibit the formation of Li dendrites in LIBs. A separator that is thermodynamically stable and strong is able to withstand the thermal runaway resulting from an internal short circuit and the mechanical penetration caused by Li dendrites [79]. For example, a commercially available separator coated with thermally conductive BN NSs effectively addresses safety concerns. It exhibits a high CE of over 100 cycles at 0.5 mA cm^{-2} in a standard organic carbonate-based electrolyte [84].

The benefits of carbon-based materials include low cost, simple processing, and a variety of shapes. Carbon-based materials are currently thought of as more realistic anode materials as a representation of the Li-ion insertion/extraction mechanism. Although graphite carbon, often known as soft carbon, has good crystallinity, its specific capacity is only 372 mA h g^{-1}. This is because Li ions intercalate into graphite carbon in stages to generate LiC_6. The drawback restricts the use of graphite carbon as a material for negative electrodes in hybrid and electric automobiles. Hard carbon, often known as non-graphite, has disorganized interior crystallites. Although it has high reversibility and capacity loss issues, it has good stability. According to studies, the main determinants of its great reversibility include particle size, additives, and high porosity. The Li-ion diffusion length can be significantly decreased thanks to the carbon's nanoscale size, which can also boost specific capacity and structural stability [85].

2.2.2 NMs for cathodes

Since the design and capacity of the majority of LIBs are cathode-constrained, optimizing LIB performance requires careful consideration of the cathode materials. In order to meet this need, cathode materials can be designed and engineered in fundamentally new and diverse ways thanks to nanotechnology. With an energy density of 800 W h kg^{-1} and a cathode capacity of only 250 mA h g^{-1}, LIBs based on insertion cathodes no longer meet the criterion of 500 km between charges for all-electric vehicles. Researchers are looking for alternative cathode materials like sulfur and oxygen that can give capacities that are orders of magnitude more than those of traditional insertion cathodes like $LiCoO_2$ and $LiMn_2O_4$ (>1,500 mA h g^{-1}) in order to increase energy density [86]. Due to its enormous advantage in specific energy (2,600 W h kg^{-1}) and capacity (1,675 mA h g^{-1}), which is five times more than that of state-of-the-art cathodes, sulfur stands out as a suitable cathode contender [87]. Additionally, one of the most prevalent elements on the globe, sulfur, is a substance that is electrochemically active, and its electron acceptance capacity per atom is up to two at 2.1 V *versus* Li/Li^+. Consequently, lithium–sulfur (Li–S) batteries have a theoretical energy density of about 2,600 W h kg^{-1}, while sulfur cathode materials have a high TC of 1,675 mA h g^{-1}. Contrary to typical insertion cathode materials, cycling causes sulfur to go through a number of compositional and structural modifications involving both soluble polysulfides and insoluble sulfides. Consequently, researchers have encountered challenges in maintaining a stable electrode structure, utilizing the active material to its maximum potential, and obtaining a sufficient cycle life to ensure excellent efficiency of the system. Although the last 10 years have seen great progress in the study of rechargeable Li–S batteries, issues with cycle life and efficiency limit their application in commercial cells. Researchers will need innovative Li–S cell designs and sulfur composite cathodes with favorable performance and characteristics to solve these enduring issues [86].

Carbon-based materials are the widely applied alternative for confining sulfur due to their high pore volume and strong electrical conductivity. Ding *et al.* [88] contributed to this field by using the simple sulfur vapor adsorption method to develop S@CNT hybrid film cathode. Conversely, a binder-free cathode has been developed from a freestanding thin-film composite consisting of sulfurized polyacrylonitrile with a conducting backbone of carbon nanotubes (CNTs) using an electrospinning technique followed by vulcanization by Razzaq *et al.* [89]. The composite material exhibited a significant preliminary discharge capacity of 1,610 mA h g^{-1} at a rate of 0.2 C and exceptional cycle stability with a discharge capacity of 1,106 mA h g^{-1} at a rate of 1 C throughout 500 cycles. In addition, Hwa *et al.* [90] fabricated a nanocomposite called cetyltrimethylammonium bromide-modified sulfur–graphene oxide–CNT (S-GO-CTA-CNT) by freeze-drying as a highly efficient cathode material. The nanocomposite exhibited efficient usage of S, with a capacity of 1,128 mA h g^{-1}. In order to introduce a straightforward, economical, and scalable method for producing micro-mesoporous structure cathodes composed of sulfur and N, S-codoped carbons, Sevilla *et al.* [91] used sodium thiosulfate and polypyrrole for homogeneously distributed sulfur throughout the carbon host. The sulfur–carbon composites have a high specific capacity of 1,100 mA h g^{-1} when subjected to a low C-rate of 0.1 C and a capacity of over 500 mA h g^{-1} when exposed to a high rate of 2 C. Furthermore, Kim *et al.* [92] designed and fabricated 3D sulfur papers that incorporate interconnected carbon materials with excellent conductivity (Figure 4a). These papers serve as flexible cathodes for Li–S batteries without the need for binders. The sulfur–carbon composite paper cathode demonstrated a notable reversible specific capacity of 1,386 mA hg^{-1}, along with a commendable rate capability of up to 5 C.

The main factor enhancing the long-term electrochemical stability of the sulfur cathode would be the electrochemical reaction restricted only to the small micropores described here. The primary factor enhancing the long-term electrochemical stability of the sulfur cathode would be the electrochemical reaction restricted only to the small micropores. In addition to porous carbon, 2D-nanostructured graphene exhibits considerable potential due to its substantial surface area and varied surface chemistry [100,101]. A sandwich-style structure, a gradient structure, unstacked graphene double layers, *etc.*, are some further examples of characteristic graphene–sulfur structures [65]. Furthermore, 1D carbon nanostructures have received a lot of attention. To enhance the electrochemical performance, sulfur-coated CNT coaxial architectures [102] and vertically aligned CNT-sulfur composites [103] have been investigated. However, it was difficult to prevent sulfur residues outside of CNTs from dissolving while cycling. The production of hollow carbon nanofibers using anodic aluminum oxide template was consequently suggested as a more successful encapsulation technique, allowing sulfur infusion to be contained solely inside the nanofibers [104]. Since a significant amount of research demonstrated that batteries using sulfur–carbon composites perform well, Zheng *et al.* [105] observed the weak interactions between polar LPS species and nonpolar carbon. Active materials are significantly detached as a result of the weak physical binding. Therefore, polar hosts are therefore favored for more powerful sulfur anchoring.

Adopting conductive polymers (such as poly-(3,4-(ethylenedioxy)-thiophene) (PEDOT), polypyrrole, polyaniline, *etc.*) as coatings or binders is another method for reducing the shuttling effect and enhancing the electrical conductivity of sulfur. Following thorough research on polymer-coated hollow sulfur nanospheres, it was discovered that PEDOT had the best electrochemical performance due to its theoretical models' predictions of its strongest sulfur binding [65]. These observations may assist in the design of sulfur electrodes for Li–S batteries to attain high capacity and long cycle life.

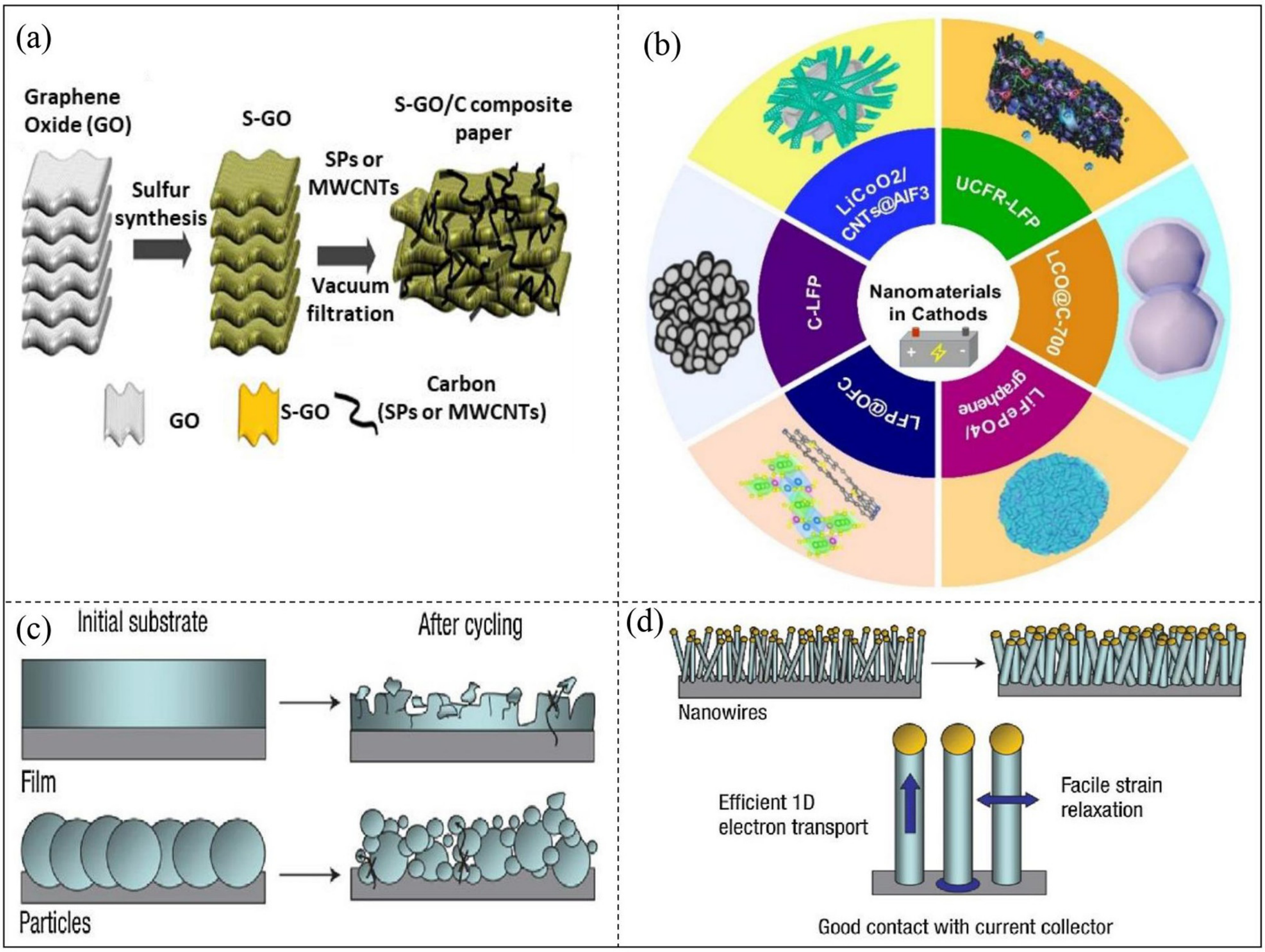


Figure 4: (a) Schematic illustration of S-GO/SP and S-GO/MWCNT composite papers. (b) Schematic illustration of various NMs applied in cathodes to achieve better ESS performance. (c) and (d) The diagram illustrates the morphological changes in Si that result from electrochemical cycling. (c) Approximately 400% volume of silicon anodes changes while cycling which tends to pulverize in Si films and particles. The arrow shows how much of the material loses contact with the current collector, which causes inadequate electron transfer. (d) After cycling, NWs evolved directly on the current collector and do not pulverize or crack into smaller particles. Instead, the NWs' facile strain relaxation enables them to expand in both length and diameter without cracking. Each NW on this NW anode is connected to the current collector, enabling effective 1D electron transport throughout the length of each NW. Reproduced with permission from (a) Kim *et al.* [92], (b) previous studies [93–98], (c) and (d) Chan *et al.* [99].

Besides this, some other materials are also used as a cathode for the LIBs. For example, $LiCoO_2$ is widely used as a cathode material. Although $LiCoO_2$ is an effective cathode material, however, cobalt is costly, as it is not available compared to other metals like iron, nickel, and manganese. In addition, $LiCoO_2$ can also fail or perform poorly when overcharged since it is not as stable as other potential electrode materials [106]. Moreover, $LiCoO_2$ activities at high voltage are impeded by increased structural deterioration and electrode/electrolyte interface breakdown. In order to address these difficulties, researchers have successfully created co-modified $LiCoO_2$ materials that combine Mg pillar structures and amorphous CoxBy with interface shielding (CB-Mg-$LiCoO_2$). This synthesis method allows for the production of cathode materials that have both high energy density and structural stability [107]. Conversely, nanostructured $LiFePO_4$ was accountable for one of the first successful alternative cathodes. This olivine demonstrates a much higher power density, longer longevity, and improved safety despite having a lower energy density than $LiCoO_2$ [108]. Consequently, $LiFePO_4$ is a highly popular cathode compound that has been commercially successful due to its excellent safety characteristics and its high TC of 170 mA h g^{-1}, even at moderate current densities [109]. For example, the fluorine-doped carbon-coated $LiFePO_4$ cathode material was innovated using polyvinylidene fluoride, resulting in the formation of a 3D conductive network structure. The structure offers benefits such as efficient electrical contact between grains, reducing the distance for Li^+ diffusion across grain interfaces, and enabling fast electron transfer during charge–discharge cycles [110]. $LiMn_2O_4$, which forms a spinel structure with manganese occupying the octahedral sites and Li primarily occupying the tetrahedral sites, is another potential cathode material. Instead of planes, like in the α-$NaFeO_2$ structure, the pathways for lithiation and delithiation in this instance are a 3D network of channels. Although $LiMn_2O_4$ is cheaper and more affordable than $LiCoO_2$, its capacity is lower than other cathodes that can be formed of α-$NaFeO_2$ structure [106]. In addition, $LiMnPO_4$ [111], Fe-doped $LiCoPO_4$ [112], $LiFePO_4$-graphene composites [113], AlF_3-coated MOF-derived $LiCoO_2$ wrapped by CNTs ($LiCoO_2$/CNTs@AlF3) [94], carbon-coated $LiFePO_4$ (C-LFP) [95], ultrahigh-capacity, fire-resistant $LiFePO_4$ [96], carbon-encapsulated lithium cobalt oxide [97], $LiFePO_4$ microparticles encapsulated in O,F-codoped carbon matrix (LFP@OFC) [98], reduced graphene oxide encapsulated Se NP (Se@RGO) [114], *etc.* NMs are also applied for cathodes to enhance the ESSs (Figure 4b). Table 2 gives a summary of energy storage NMs as well as their morphologies, synthesis strategies, and electrochemical performances.

2.3 Energy distribution

The significant losses that occur during power distribution can be lessened with the aid of nanotechnology. Electricity cables and power lines can be made using nanoparticles' exceptional electric conductivity, such as CNTs. Microwaves and lasers are two examples of wireless energy delivery that use nanotechnology [124]. Moreover, superconductive materials can be improved using nanotechnological methods for lossless current conduction. Electricity systems with dynamic load and failure management, demand-driven energy supply with adjustable price mechanisms, and the ability to feed through a variety of decentralized renewable energy sources are all necessary for the distribution of electricity in the future. Nanotechnologies, including nano-sensory sensors and power electronic components capable of handling the extraordinarily complicated control and monitoring of such grids, could make a significant contribution to the realization of this goal [57]. Si NPs could be a useful and attractive material in energy distribution because researchers have shown that Si anodes have a ten times higher charge density and a low discharge potential than carbon and other oxides and nitrite anodes. However, Si bulk films and micron-sized particles employed as electrodes in Li batteries have shown capacity fading and short battery lifetime due to pulverization and loss of electrical contact between the active material and the current collector (Figure 4c). To overcome the limitation, Chan *et al.* (2008) synthesized Si NWs on stainless steel substrates using gold catalysts. The synthesized NWs featured short Li insertion lengths, good electronic contact, and conduction and stood up to high strain instead of pulverization (Figure 4d). In contrast to anodes made of bulk silicon, these researchers discovered that silicon NWs do not crack even if they swell as Li ions are absorbed upon a battery's discharge and contract as they leave during a battery's recharge [99].

2.4 Energy usage

In addition to the efficient use of existing energy sources, increasing energy efficiency and reducing needless energy usage are required to establish a sustainable energy supply. This holds true for both individual families and all sectors of industry. Numerous strategies for energy conservation are offered by nanotechnologies. For example, NMs could play a significant role in reducing the fuel consumption of automobiles by (i) developing nanocomposites-based underweight construction materials for vehicles, (ii) optimizing fuel combustion through wear-resistant, lightweight

Table 2: Summarization of energy storage NMs as well as their morphologies, synthesis strategies, and electrochemical performances

Materials	Morphology	Synthesis method	Applications	Capacity (mA h g^{-1})	Current density (A g^{-1})	Rate-C	CE (%)	Cycle numbers	Ref.
SiO_2	Nanotubes	Magnesiothermic reduction	Anode	712.7	5	—	81.78	400	[71]
NiCo-MOF	NS	One-pot hydrothermal synthesis	Anode	100.18	5	—	81.0	3,000	[58]
SiOC/Sb	Nanocomposite	Pyrolysis	Anode	74.4–2,232	2.23	—	76	200	[59]
Cr/MoS_2	Nanohybrids	Electrostatically driven self-assembly	Anode	>900	0.2	—	—	50	[60]
$C\text{-}TiO_2$	Nanohybrids	Hydrothermal treatment	Anode	718	—	2	81.3	300	[61]
Si–C	Composite	Liquid milling process and pyrolysis	Anode	1,600	—	—	80	100	[66]
Si	Interconnected hollow nanosphere	Template-based	Anode	2,725	2.2	—	99.5	700	[115]
Si	Nest-like Si nanospheres	Solvothermal method	Anode	3,628	0.4	—	72.7	48	[116]
Si	Micropillar structures	Photolithographically	Anode	2,600	—	0.33	99	100	[72]
$SiO_2@a\text{-}TiO_2@Ag$	Composite	Sol–gel method	Anode	1,320	0.1	—	58	300	[78]
Si-C	Porous structured composite	Magnesiothermic reduction	Anode	~1,467	2.6	—	—	370	[117]
$LiCoO_2$	Nanocomposite	*In-situ* construct	Cathodes	180	—	0.5	91	200	[118]
$Al@LiMn_2O_4$	Composite	Simple combustion	Cathodes	100.7	—	0.5	93.9	400	[119]
S@CNT	Hybrid film	—	Cathodes	1,145	—	0.2	99	100	[88]
SPAN-CNT	composite	Electrospinning	Cathodes	1,314	—	1	100	250	[89]
S-GO-CTA-CNT	Nanocomposite	Freeze drying	Cathodes	1,128	0.8	—	99.3	80	[90]
S@C	Composite	Fabrication process	Cathodes	1,100	—	0.2	98	260	[91]
S-GO	3D Composite	Chemical synthesis	Cathodes	1,386	—	5	~100	400	[92]
$LiMn_2O_4/GO$	Nanocomposite	Hydrothermal route and solid-state reaction	Cathodes	130	—	0.05	98%	100	[120]
$C@SnO_2\text{-}rGO\text{-}SnO_2$	sandwich-like mesoporous NSs	Fabrication process	Cathodes	1,211	0.2	—	99	300	[121]
Fe_3O_4-NC	Composites	Polymerization-assisted synthesis	Cathodes	1,316	—	0.2	100	1,000	[122]
CB-Mg- $LiCoO_2$	Composites	*In situ* co-precipitation and electroless plating	Cathodes	185.5	—	1	94.93	100	[107]
$LiFePO_4$@FC	Nanocomposite	Ball-milling assisted rheological phase method combined with a solid-state reaction	Cathodes	100.2	—	20	—	1,000	[110]
$LiMn_2O_4$-GO	Nanocomposite	—	Cathodes	110	—	0.5	97	150	[123]
LiMnPO4/C	Nanocomposite	Solution combustion	Cathodes	126.9	—	0.05	93.8	50	[111]
$Fe@LiCoPO_4$	Nano-plates	Doping and high-temperature annealing	Cathodes	138	—	0.1	93	300	[112]
$LiFePO_4$/graphene	Composites	—	Cathodes	160	—	0.2		80	[113]
$LiCoO_2/CNTs@AlF_3$	Composites	Annealing and wrapping	Cathodes	120	—	2	98	500	[94]
$C@LiFePO_4$	Composites	Liquid carbon dioxide-based coating	Cathodes	168	—	0.1	100	1,000	[95]
$LiFePO_4$	Nanocomposite	Bottom-up self-assembly strategy	Cathodes	108	—	2	—	315	[96]
$LiCoO_2@C$	Composites	Fabrication and coating	Cathodes	171.1	—	1	92.5	200	[97]
$LiFePO_4$@OFC	Composites	Solid-state sintering	Cathodes	160.9	—	1	100	500	[98]
Se@RGO		Self-assembly process	Cathodes	265	—	0.2	100	200	[114]

engine components, nano-fuel additives, and low rolling resistance tires [57]. Nanotechnology may also be able to increase energy efficiency and decrease wasteful use, which will help ensure a sustainable energy supply. Materials that are wear-resistant, lightweight, anti-corrosive, *etc*., can be manufactured using nanotechnology to ensure that they are best suited for the job at hand. This has an impact on everything from building and construction technology, insulation, and lighting to better fuel combustion [125].

There is every reason to expect that advances in technology like fuel cells and solar cells that could help us become less dependent on fossil fuels, such as nano-based technologies, offer substantial prospects for assisting in the achievement of desirable environmental objectives. Our energy systems can benefit from finding a mechanism to store energy-dense gases. Highly porous organic matrices known as MOFs are capable of storing natural gas or hydrogen. The cube-shaped nanostructures are made of an organometallic framework, and their interiors are lined with many pores with a diameter of a few nanometers. The surface area of nanopores is large. These structures may also serve as power sources for many gadgets, including laptops. Small fuel cells might be used as a form of rechargeable storage. Furthermore, the functioning of lighting in our homes and places of employment today consumes enormous quantities of energy. Nanotechnology-based lighting technologies would significantly improve the environment [126].

3 Methods of NM-based ESS patent search

The Lens website (https://www.lens.org/) was used to retrieve the patents on NM-based BESS as well as these patents were used for analysis and landscape review. The Lens is an open worldwide cyberinfrastructure to improve the effectiveness, fairness, transparency, and inclusivity of the innovation system. The LENS provides access to virtually all the global patent documents as freely accessible, annotated digital universal materials that combine technical and scholarly literature as well as regulatory and commercial information. To create an open map of global knowledge-driven innovation, the Lens enables the sharing, aggregation, and embedding of document collections, aggregates, and analysis [127]. The LENS includes 146.1 million patent documents from over 106 jurisdictions. The extraction methods of NM-based BESS patents are described below.

3.1 Research design structure

To explore the relevant patents from the Lens database, specific keywords were used including "energy storage system," "battery," and "nanomaterial." The Boolean operator "AND" was applied to connect the above keywords to search for appropriate patent documents on the Lens website. The patent searches were conducted on the last week of May 2023 without filtering the year of publication. The patents are then screened, and only those belonging to the NM-based BESS simple family are chosen. A simple patent family is a group of patent applications that collectively are thought to cover a single invention. The applications' technical content is regarded as being similar. Every member of a simple patent family will have the same priority. In most cases, the family mode is more suitable, as PLAs typically based on distinct inventions represented by a collection of documents compiled into a patent family [128]. Finally, multiple selection and exclusion criteria are employed to obtain the final patent database of NM-based BESS for study.

3.2 Selection procedure

Published patents related to NM-based BESS were retrieved from the United States, World Intellectual Property Organization (WIPO), and European Patent databases by applying keyword searches using Lens software. Only the patent documents pertaining to the NM, nanocomposites, NM colloids, and nanocomposite colloids are considered throughout the analysis. Searches are conducted using keywords on the Lens website, and the most relevant patent documents are retrieved through step-by-step searching. First, the keyword "energy storage system" was used, and a total of 2,032,461 (n = 2,032,461) patents were retrieved. Next, "battery" was applied in the titles and abstracts, and a total of 193,601 (n = 193,601) patents were found. Finally, we searched "nanomaterial" in the titles and abstracts to further refine the patent numbers and came up with a total of 255 (n = 255) patents. Following that, only the simple family of patents was chosen, and a total of 132 (n = 132) patents were taken into account.

The selected patents of the simple family were verified based on relevant International Patent Classification (IPC) and Cooperative Patent Classification (CPC) codes. B82Y (specific uses or applications of nanostructures; measurement or analysis of nanostructures; manufacture or treatment of nanostructures), Y02E 60/10 (Energy storage using batteries), and H01M (processes or means, *e.g.*, batteries, for the direct conversion of chemical energy into electrical energy) codes were used to screen the retrieved documents and a total of 24 patents were excluded due to mismatches with the relevant codes. Therefore, a total of 108 (n = 108) patents were found for further analysis. After extensive reviews, 12 patents were disregarded because they were duplicates (same patent with different patent numbers), while another 7 were excluded due to not being relevant. Finally, a total of 89 patent documents were obtained for the PLA on NM-based BESS. The complete patent selection procedures are illustrated in Figure 5.

3.3 Generating graphic representations and analyzing patent data

After screening, a total of 89 patents were found to analyze data from related innovations at strategic, competitive, and technological levels using statistical and analytical charts. The data were subsequently extracted and analyzed using Microsoft Office Excel. The data that were obtained was subsequently organized into a spreadsheet and dashboard created in Microsoft Excel. This compilation included many pieces of information, such as the Title, Abstract, Application

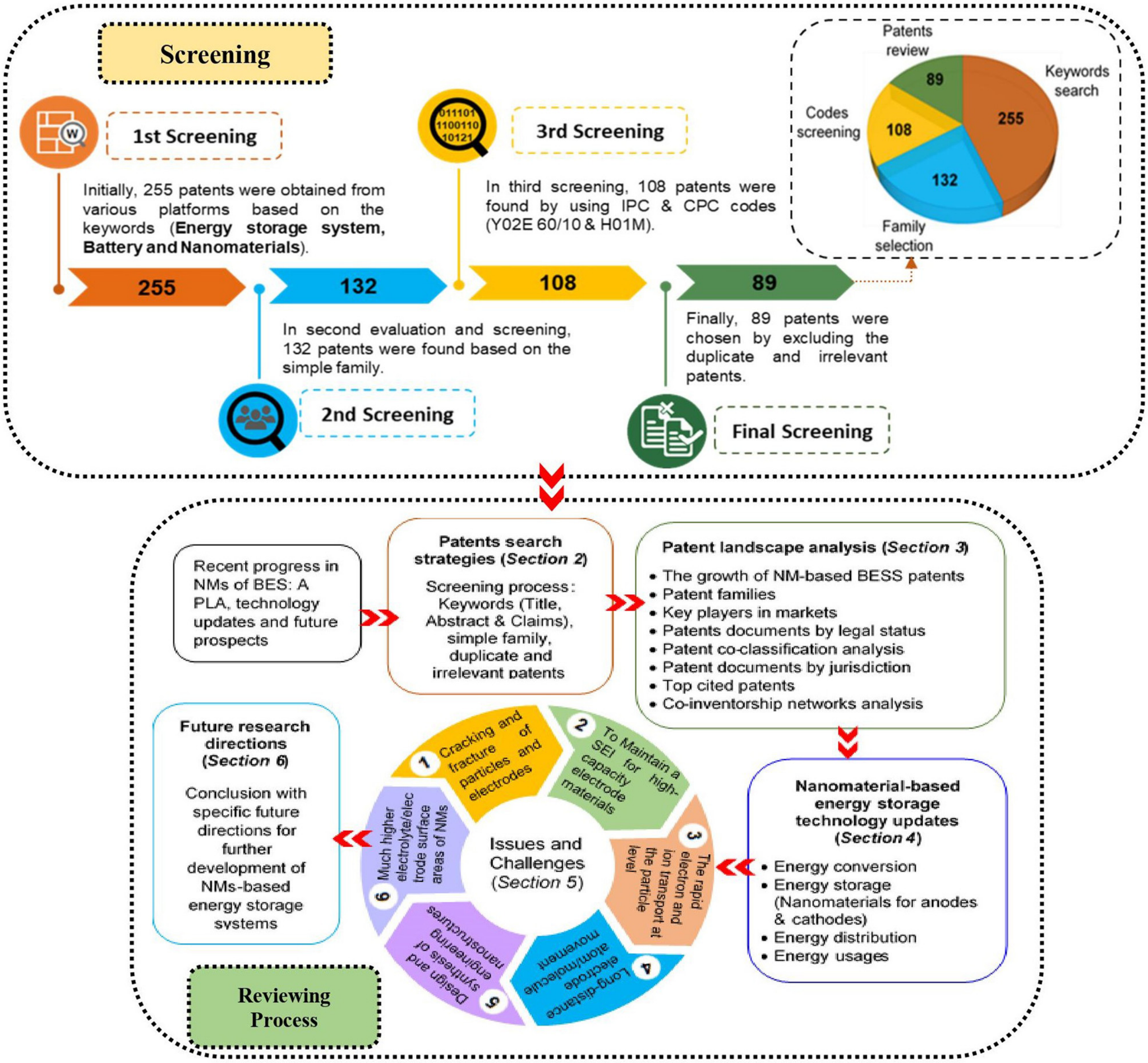


Figure 5: Graphical illustration of the search strategy and review findings in the present study.

Number, Inventors, Publication Date, Application ID, and Applicants. Subsequently, a comprehensive examination was conducted on all facets of the listed patents, followed by a meticulous categorization process to assign them to their respective categories [129]. The obtained patent information was analyzed in various parameters including patent growth, key players in the markets, legal status, patent co-classification, top cited patents, and co-inventorship network. Table 3 presents a summary of key features in highly cited 60 patents among the selected documents.

3.4 Limitation

A popular technique for analyzing a specific field of research, assessing the consequences on other fields, and appraising current advancements is PLA. Identifying and tracking patents is challenging work. Therefore, it is important to be aware of some potential limitations in our analysis. The first limitation has to do with the method of searching for pertinent patents. When researching mostly specific areas of study, using keywords can be complicated because an adequate number of unrelated patents end up in the sample [130]. Consequently, a comprehensive review of retrieved documents should be conducted to avoid irrelevant patents. An in-depth manual screening of the documents might reveal that there are just a few instances of patent documents being included that are unrelated to the designated technical field. Second, patent documents that are not included on the Lens website are likely to be missed. Future recommendations could include more publicly accessible patent databases, including the Derwent World Patent Database and the Scopus database. Third, the analysis did not include patents that might have been relevant to NM-based BESS but did not have any of the keywords in their titles, abstracts, or claims. Fourth, the study of the database only takes into account simple patent families. Overall, an understanding of global research, commercialization structures, and market trends under a specific field of research using PLA is highly critical.

4 PLA

This article attempts to briefly introduce and discuss the crucial role of patents in current advanced societies related to the production of batteries. Considering the significance of the role played by patents in the commercialization, promotion, and protection of information in all technical sectors, including the provision of ESDs, like batteries.

4.1 The growth of NM-based BESS patents

The number of patent applications filed throughout time that have an eternal impact on the related field for potential future study and research advancement is referred to as the growth of patents. Academic and business research increasingly use patents to protect their inventions. Consequently, patenting has grown substantially over the past few decades. For instance, patent documents under NM-based BESS also increased gradually over time. All generated patents fall into three categories such as published, filed, and granted. To determine overall growth, patents from these three groups have been combined and presented in Figure 6a. Conversely, these three groups (published, filed, and granted) have also been depicted separately (Figure 6c). In addition, patent applications and granted categories are shown in Figure 6b. The growth rate was stable up to 2008, and it started to rise from 2010 (Figure 6a). The number of patents increased from 2 in 2010 to 7 in 2012. After that, the number of patents gradually decreased to 2 in 2015; however, it increased again to a maximum (11) in 2020. Conversely, the aggregate diagram (Figure 6c) compares the numbers of NM-based BESS patent documents by published, filed, and granted date in each year until 2023. The numbers for all kinds of patents gradually increased over time. The upward trend began in 2009 and reached a peak in 2018. The highest number was under filed with 13 patents in 2018, the next rank was for published patents with 11, and patents under granted categories were 6 in 2020. Overall, an upward trend of the NM-based BESS patents was observed. In contrast, Figure 6b clearly shows that the number of patents granted was 15 (17%), which was much less than that of the applications (74; 83%). This is because it takes approximately 3 years to get a patent from the patent office. Because the USPTO organizes patent applications depending on the technology of the invention and assigns patents to technology groups of examiners at the USPTO for examination, some technical areas have a longer or shorter wait period.

4.2 Patent families

A patent family is a set or compilation of patent applications that cover the same or related technical material, while there is no one definition for what a patent family is, and patent families frequently differ from database to database. One of the primary objectives of patent families was to make it simpler for people who like analyzing patent data to quickly identify patents connected to or related to a certain innovation from anywhere in the

Table 3: A summary of key features of the selected highly cited patents among the retrieved documents in the field of BESS

Ref.	Publication year	Inventors	Contribution	Document type	Jurisdiction	Cited by patent count	Legal status
[131]	2002	Yadav Tapesh; Hu Hongxing	Nano-ionic products and devices	Patent application	US	7	Expired
[132]	2003	Yadav Tapesh; Au Ming	Nanotechnology for electrochemical and energy devices	Granted patent	US	48	Expired
[133]	2005	Yadav Tapesh; Pfaffenbach Karl	Slurry processing of nanoscale materials into nanotechnology products	Patent application	US	10	Discontinued
[134]	2008	Defries Anthony; Brongersma Mark	A method or means to use or combine plasmonic, thermal, photovoltaic, or optical engineering	Patent application	WO	13	Pending
[135]	2010	Lam Lan Trieu; Furukawa Jun	Energy storage device	Patent application	US	111	Active
[136]	2010	Stroemme Maria; Nyholm Leif; Mihranyan Albert	Composite materials including an intrinsically conducting polymer, and methods and devices	Patent application	US	16	Inactive
[137]	2011	Ban Chunmei; Wu Zhuangchun; Dillon Anne C	Method of fabricating electrodes including high-capacity, binder-free anodes for LIBs	Patent application	WO	4	Pending
[138]	2011	Farmer Joseph C	High-performance rechargeable batteries with fast solid-state ion conductors	Patent application	WO	1	Pending
[139]	2011	Hu Liangbing; Choi Jang Wook; Yang Yuan; Cui Yi	Conductive fibrous materials	Patent application	US	26	Active
[140]	2011	Irvin Randall T; Barkeloo Jason E; Hassett Daniel J	Improved microbial fuel cell	Patent application	WO	2	Pending
[141]	2011	Cui Li-Feng; Cui Yi; Hu Liangbing	Methods for production of nanotube-based NM membrane exfoliated CNTs	Patent application	US	65	Inactive
[142]	2011	Bosnyak Clive P; Swogger Kurt W	Methods for the production of exfoliated CNTs	Patent application	US	33	Active
[143]	2012	Walters Ian; Williams Martin	Methods of processing particulate carbon material, such as graphitic particles or agglomerates of carbon nanoparticles such as CNTs	Patent application	WO	33	Pending
[144]	2012	Lu Wen	High-performance batteries with carbon NMs and ionic liquids	Granted patent	US	35	Inactive
[145]	2012	Nazri Gholam-Abbas	Method of depositing silicon on carbon NMs and forming an anode for use in LIBs	Patent application	US	97	Discontinued
[146]	2012	Han Wei-Qiang	Method of synthesis of carbon-coated Magneli-phase tino 2n −1 NMs	Patent application	US	25	Discontinued
[147]	2012	Burton David J; Lake Max L; Nazri Maryam; Palmer Andrew C	Method of depositing silicon on carbon NMs	Patent application	US	115	Discontinued
[148]	2012	Liu Jun; Cao Yuliang; Xiao Lifen; Yang Zhenguo; Wang Wei; Choi Daiwon; Nie Zimin	NMs for sodium-ion batteries	Patent application	US	11	Inactive
[149]	2012	Wang Xiao-Liang; Han Weiqiang	Method of synthesis of intermetallic m-sn5 (m = Fe, Cu, Co, Ni) compound	Patent application	WO	15	Pending

(Continued)

Table 3: *Continued*

Ref.	Publication year	Inventors	Contribution	Document type	Jurisdiction	Cited by patent count	Legal status
[150]	2014	Chen Zhongwei; Fowler Michael; Zarrin Hadis	Highly ion-conductive nano-engineered porous electrolytic composite membrane for alkaline electrochemical energy systems	Patent application	WO	7	Pending
[151]	2014	Yazami Rachid; Darolles Isabelle M; Weiss Cedric M	Lithium-ion fluoride electrochemical cell	Patent application	US	24	Discontinued
[152]	2014	Suib Steven L; Huang Hui; Xu Linping	Power storage devices using mixed-valent manganese oxide	Patent application	WO	6	Pending
[153]	2014	Tyler Matthew R; Obasih Kem M	Polymerized LIB cells and modules with permeability management features	Patent application	WO	1	Pending
[154]	2014	Worsley Marcus A; Baumann Theodore F; Satcher Jr Joe H; Stadermann Michael	Porous substrates filled with NMs	Granted patent	US	24	Active
[155]	2014	Ruediger-Bernd Schweiss; Schumann Lea; Hammer Christian	Method for producing coated active materials, core, and battery	Patent application	US	5	Active
[156]	2015	Singh Neelam; Galande Charudatta; Mathkar Akshay; Reedy Arava Leela M; Ajayan Pulickel M; Vlad Alexandru	Methods of making multilayer energy storage devices	Patent application	US	35	Discontinued
[157]	2015	Suib Steven L; Huang Hui	Methods for preparing substrate cored-metal layer shelled metal alloys	Patent application	US	5	Discontinued
[158]	2016	John Vijay; Mcpherson Gary	Hollow nanoparticles with hybrid double layers	Patent application	US	28	Discontinued
[159]	2016	Roberts Aled Deakin; Wang Suxi; Zhang Haifei; Li Xu	Method of preparing a porous carbon material	Patent application	WO	15	Pending
[160]	2016	Tanimola Olanrewaju W	Methods for synthesis of graphene derivatives and functional materials from asphaltenes	Patent application	US	14	Active
[161]	2016	Fong Wenmei Eileen; Yan Qingyu Alex; Zhou Yanping; Rui Xianhong; Lu Yan	Biochemistry-derived carbonaceous metallics frameworks for use in batteries	Patent application	WO	9	Pending
[162]	2016	Chen Yu-Chen; Zhong Guoming	Efficient NMs manufacturing process and equipment	Patent application	US	7	Discontinued
[163]	2017	Lu Yi-Chun; Wang Zengyue; Tam Long Yin Simon; Zou Qingli; Cong Guangtao	High-energy density and low-cost flow electrochemical devices	Patent application	WO	1	Pending
[164]	2017	Kotov Nicholas A; Zhu Jian; Tung Siu On	Gels and nanocomposites containing aramid nanofibers	Patent application	WO	5	Pending
[165]	2017	Babenko Vitaliy; Grobert Nicole	Porous materials comprising two-dimensional NMs	Patent application	US	35	Active
[166]	2017	Zhou Chongwu; Fang Xin; Ge Mingyuan; Rong Jiepeng	Free-standing active material/carbon NM network film as light-weight and high-power electrodes for LIBs	Granted patent	US	2	Active
[167]	2017	Jin Jifan	Air metal fuel cell	Patent application	US	15	Active

(Continued)

Table 3: *Continued*

Ref.	Publication year	Inventors	Contribution	Document type	Jurisdiction	Cited by patent count	Legal status
[168]	2018	Johnson Paige L; Neff Jonathan G	Synthesized, surface-functionalized, acidified metal oxide (AMO) materials for energy storage applications	Patent application	US	1	Active
[169]	2018	Hass Jamie Lynn	Integrated electrode-electrolyte unit	Patent application	US	1	Active
[170]	2018	Yoon Yeo-Heung; Lee Hyo-Young; Kwon Soon-Geun; Choi Jae-Young	Electrode structure having rolled graphene film	Granted patent	US	1	Active
[171]	2018	Matsumura Taku; Mikami Jun	Fibrous carbon NM-based conductive paste composition for the secondary battery electrode	Patent application	US	11	Active
[172]	2018	Hu Liangbing; Wachsman Eric; Liu Boyang; Gong Yunhui; Fu Kun	Methods for the synthesis of solid-state hybrid electrolytes	Patent application	WO	35	Pending
[173]	2018	Hong Sanghyun; Jung Yung Joon; Lavall Rodrigo Lasserote; Kim Hyehee; Busnaina Ahmed	Solid-state integrated electrode/electrolyte system	Patent application	US	7	Discontinued
[174]	2018	Coleman Jonathan; Kelly Adam; Hallam Toby; Duesberg Georg	Method for the synthesis of a multi-layer device structure comprising an active layer of material and an insulating layer of material	Patent application	WO	4	Pending
[175]	2019	Yushin Gleb; Turcheniuk Kostiantyn; Benson James	Method of synthesizing a material exhibiting desired microstructure characteristics based on chemical dealloying one or more group I or group II elements from an alloy and method of synthesizing nanocomposites	Patent application	US	12	Active
[176]	2019	Boies Adam Meyer; De Volder Michael Franciscus; De La Verpilliere Jean Leclerc; Graves Brian	Manufacture of composite nanostructures	Patent application	WO	6	Pending
[177]	2019	Rohani Parham; Swihart Mark	Method of synthesizing silicon-carbon NMs	Patent application	WO	8	Pending
[178]	2019	Liu Yunyang; Odeh Ihab N	Method of synthesizing carbon encapsulated sulfur-metal oxide composite	Patent application	US	8	Discontinued
[179]	2019	Huayu Sun; Yuli Li	Negative electrode structure for secondary battery and secondary battery incorporating same	Patent application	US	2	Discontinued
[180]	2019	Janowska Izabela; Truong-Phuoc Lai; Ba Housseinou; Pham-Huu Cuong	Method of synthesizing colloidal NM/polymolecular system nanocomposites	Patent application	US	6	Discontinued
[181]	2020	Johnson Paige L; Neff Jonathan G	Synthesis of AMO and their application in battery electrode	Granted patent	US	2	Active
[182]	2020	Aria Adrianus I; Gharib Morteza	CNTs – graphene hybrid structures for separator free silicon – sulfur batteries	Granted patent	US	1	Active
[183]	2020	Ying Jackie Y; Yang Jinhua; Zaghib Karim; Trudeau Michel L	Core-shell NPs and their use in electrochemical cells	Patent application	US	3	Pending
[184]	2020	Gleason Karen; Wardle Brian; Cohen Estelle; Zhou Yue; Wang Xiaoxue; Stein Yosef	Method of synthesizing supercapacitors and other electrodes	Patent application	WO	1	Pending

(Continued)

Table 3: *Continued*

Ref.	Publication year	Inventors	Contribution	Document type	Jurisdiction	Cited by patent count	Legal status
[185]	2020	Cross Danny; Kirby Larry Herbert; Bailey Thomas Frank	Surface area and porosity for catenated carbon nano-onions (cnos)	Patent application	US	1	Active
[186]	2020	Johnson Paige L	Blended active materials for battery cells	Patent application	US	1	Discontinued
[187]	2021	Belcher Angela; Qi Jifa; Wei Shuya	High-energy rechargeable Al-CO_2 battery for CO_2 capture/conversion and electric power generation/storage	Patent application	US	4	Pending
[188]	2021	Ho Kam Piu; Jiang Yingkai; Sun Xinying	Conductive composition for secondary battery	Patent application	WO	1	Pending
[189]	2022	Skoptsov George L; Zeller Kurt W; Mantri Aayush; Viswanathan Vignesh	Nanocarbon material and applications of nanocarbon material	Patent application	US	1	Pending
[190]	2022	Johnson Paige L	Alkaline and AMO blended active materials	Patent application	US	1	Pending

world. The use of patent families is also advantageous when doing patent searches and extracting patent data from numerous patent offices. In order to connect the patent applications in a patent family, priority claims are frequently used [191].

4.3 Key players in markets

Market actors' ways are evolving as a result of the changing nature of innovation, the globalization of markets, the fragmentation of industrial value chains, and the development of new players. In order to maximize the balance between private and social advantages and support economic progress and societal welfare, patent systems are constantly evolving [192]. In Figure 7, the top ten innovators, owners, and applicants are shown to identify the leading organizations in the NM-based BESS market. Among the ten innovators, Johnson Paige L was in the first position by contributing nine patents (Figure 7a). Between the remaining inventors, two inventors have three patent documents each, and the rest seven inventors have two patent documents each. In contrast, Hheli LLC was in first position in both owners and applicants contributing nine and ten patents, respectively (Figure 7b and c). The second top owner was Nanoproducts Corporation patenting three documents. California Institute of Technology, Massachusetts Institute of Technology, Ppg Industries Ohio INC, and The Board of Trustees of the Leland Stanford Junior University each possesses two patents. The rest of the owners have one patent each. In contrast, Massachusetts Inst Technology came in second applicant having three patents. Other applicants have two patents each.

4.4 Patent documents by legal status

The legal status of patents has not been taken into consideration in most PL studies. The inclusion of patents that are no longer valid legally makes it seem evident that conclusions from such studies could result in incorrect interpretations [193]. Patents are divided into six groups based on their legal status, including active, inactive, pending, discontinued, expired, and unknown patents. The active patent is the patent that has been approved or granted; the owner can implement or monetize from it in accordance with its strategy. Conversely, inactive patents are, to put it simply, patents that are no longer in effect. These patents have expired, been abandoned, or been withdrawn. The inactive patents are no longer enforceable or commercially viable. This indicates that the patent holder no longer has the right to use the patent exclusively. Anyone may utilize the patent after it is released into the public domain [194]. A patent pending is an obvious sign of an inventor's desire to protect their concept and indicates the beginning of the process of applying for the sole right to use, sell, or license their creation. There is no inherent legal significance to a patent pending notice. At that moment, neither the product nor the technique is legally protected. In addition, it proves that a patent application has been submitted, in which case it would take precedence over any later-filed patent application for a nearly identical idea. Companies generally use a closed patent strategy intended to protect and extend the utilization of existing inventions from commercial competitors. The length of a patent's term determines how long it can remain in effect. It might differ depending on the jurisdiction and the type of patent, but it is typically given in years beginning either with the filing date for the patent or with the date the patent was granted. The majority of jurisdictions require ongoing payment of maintenance or renewal fees to keep a patent in effect. When a patent's maximum term expires or the grant holder fails to pay the renewal fee on time, the patent is considered to be

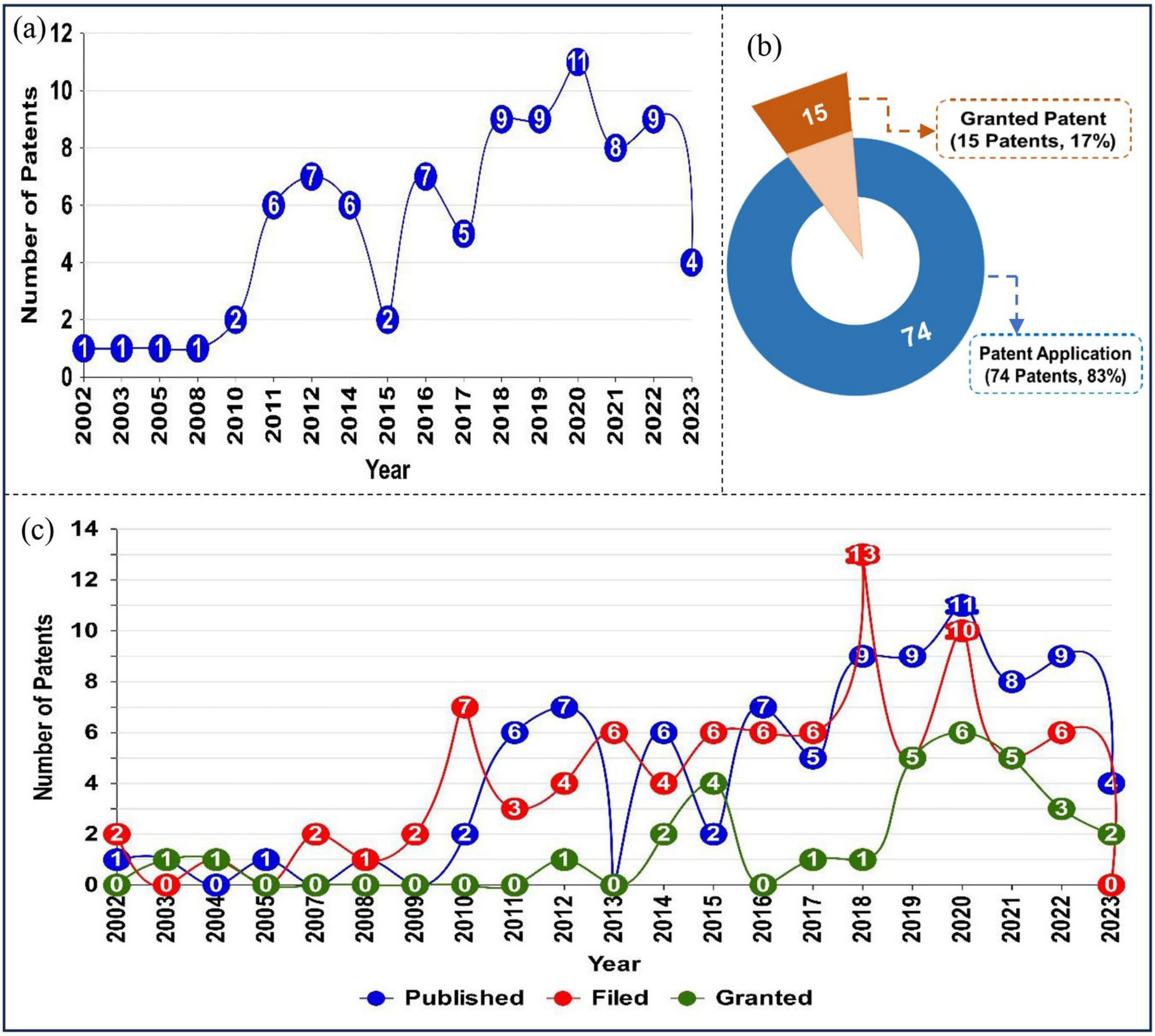


Figure 6: The overall growth of patent documents under NM-based BESS. (a) The growth of generated patents from three groups (filed, granted, and published) by year, (b) the number of patent applications and granted patents, and (c) the number of patents in each group (filed, granted, and published).

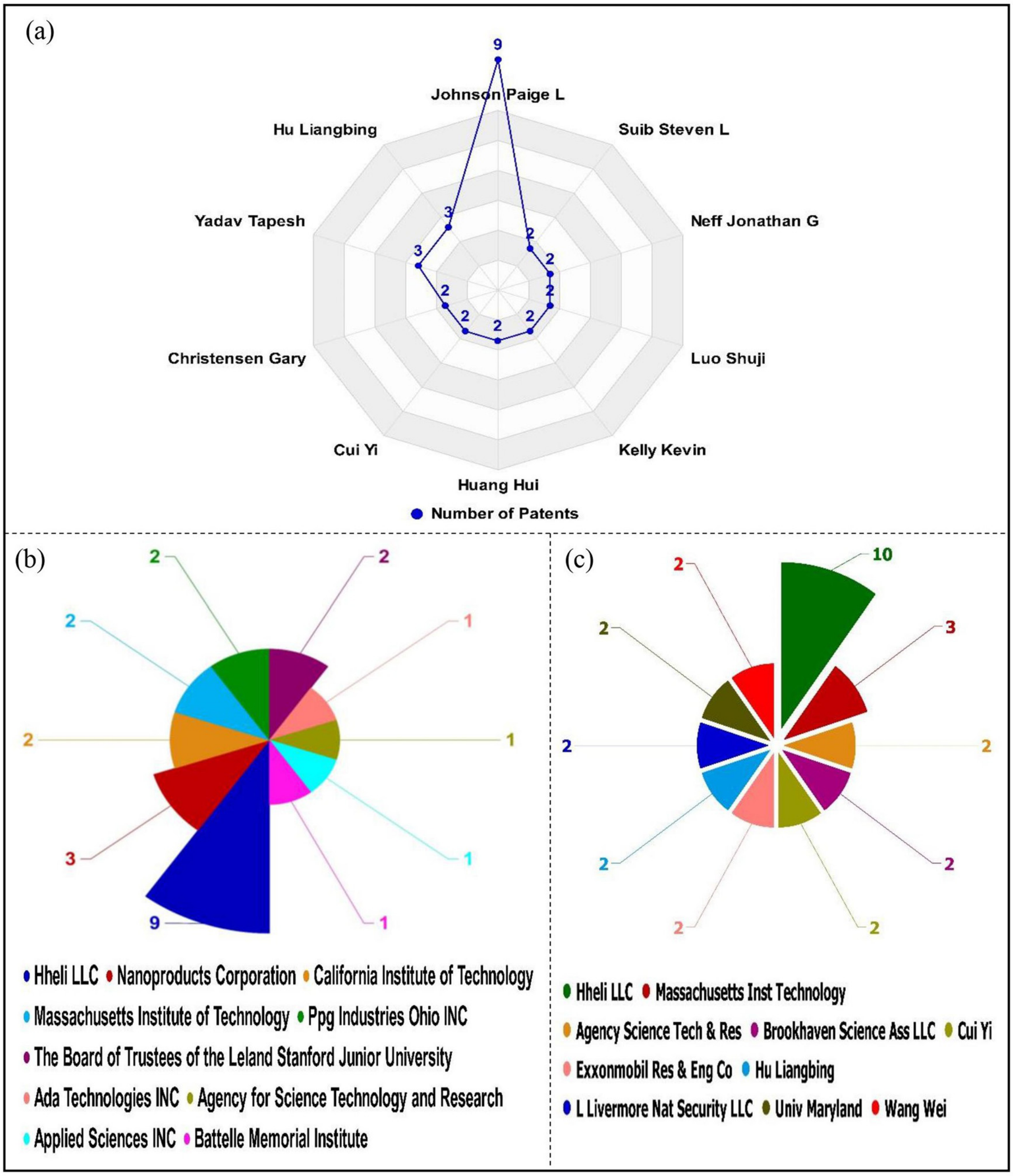


Figure 7: Key players in the market for patent documents registered under the NM-based BESS. (a) Top ten inventors, (b) top ten owners, and (c) top ten applicants.

expired. The term discontinued patent refers to a patent that is no longer continued (rejection, withdrawal, refusal, *etc.*) and can be revived. Unknown patents are those that the requester is unaware of or does not recognize. The 89 patents that were registered in the NM-based BESS application are shown in Figure 8a in terms of their level of legal protection status. The pending group had the highest number of patents, 38 in total (43%), while the number of active patents was 27 (30%). This is because, based on the complexity of the invention, this stage of the patent process may take 1–3 years or longer. For example, patent applications under software or electronics commonly have patents pending for 5 years or longer. In addition, the length of time the patent is pending can also be influenced by the USPTO's backlog of applications and the complexity of the invention [195]. In contrast, discontinued patents took up the following position, with 19 numbers. Conversely, the number of inactive and expired patents was very low, consisting of 3 and 2, respectively.

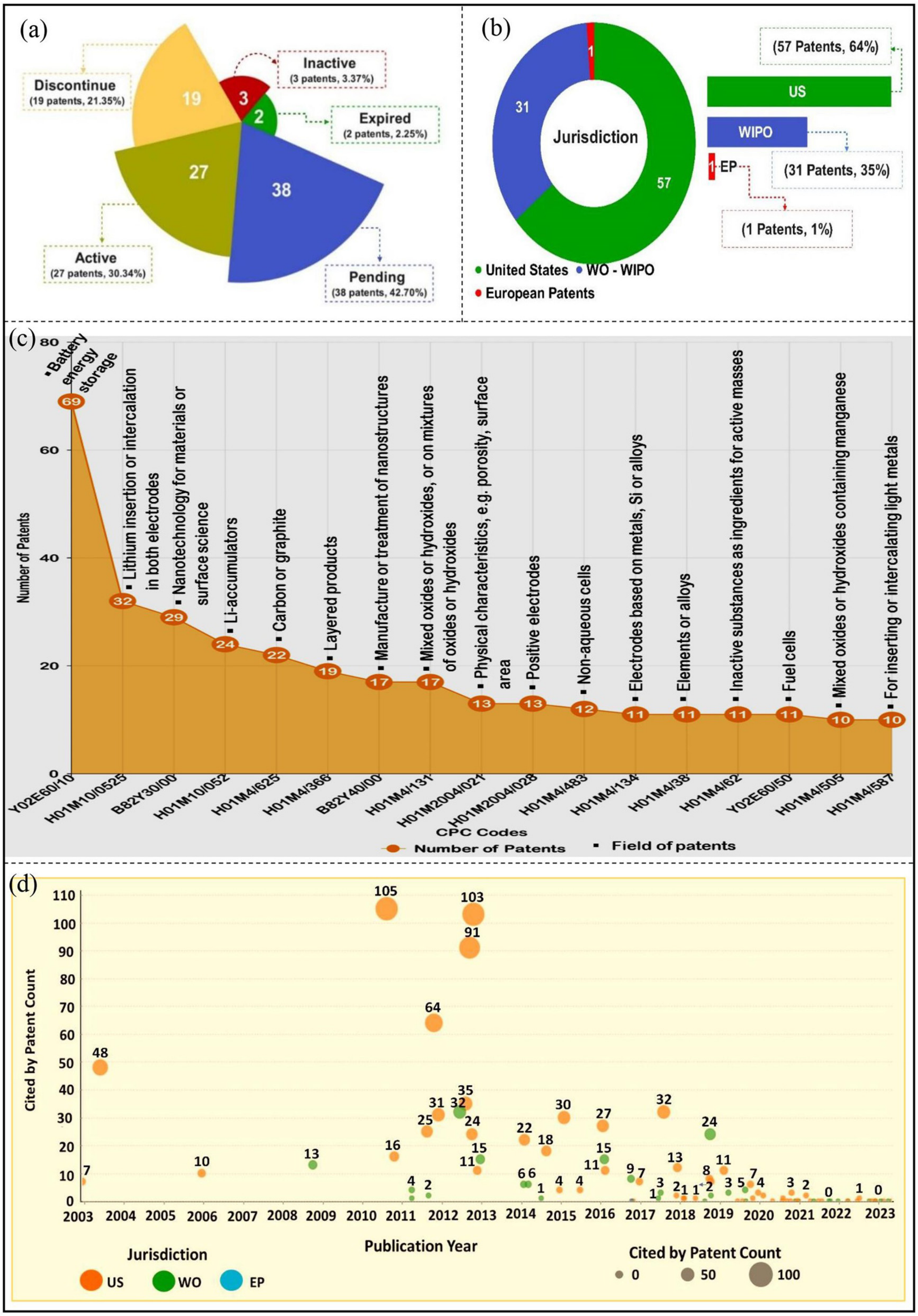


Figure 8: Number of NM-based BESS patent documents under different legal status groups (a), various Jurisdictions (b), each CPC code (c), and the top-cited patent by year (d).

Both granted and pending patents are covered by legal protection. The term “granted patents” refers to patents that at least one patent authority has approved for registration. Patents that have been granted have undergone examination and approval by the Patent Office, placing them in a high position in terms of technical expertise and potentially qualifying them as technically sound patents.

4.5 Patent documents by jurisdiction

Patent jurisdiction refers to the convention nation and/or area in which the expected patent has already been filed or approved or will be filed or approved and for which the licensee will pay for the prosecution, application, defense against illegal attempts, and maintenance. According to the data shown in Figure 8b, all of the registered patents in this field have been registered in three different jurisdictions. The United States holds the top position in patent jurisdiction for this topic with 57 patents (64%) that have been registered there. The WIPO was listed next in rank; 31 patents (35%) were registered under this jurisdiction. Conversely, only 1% of patents was registered under European patents jurisdiction in NM-based BESS. It is noted that the place of registration can be a sign of both the country consuming the technology and the country producing it, depending on whether the knowledge holders want to file their patent in their own country or in a country other than the one where the technology was created [4].

4.6 Patent co-classification analysis based on the IPC code

A fresh understanding of the relationships and underlying interaction dynamics of knowledge domains within a particular technology domain can be gained through an analysis of co-occurring patent classification codes. Patent categorization codes can be used to establish the interconnection of knowledge sectors, analogous to how technological knowledge flow is measured. In general, the degree of knowledge interaction dynamics between two patent categorization codes is reflected by how frequently those codes co-occur in patent documents. As a result, it can make it easier to understand intuitively how technological knowledge bases are interconnected and how they affect PL [196]. The main and most crucial purpose of the patent application is to prevent competitors from copying newly developed innovations. A system using distinctive codes like IPC and CPC is used to categorize patents into various technological fields, providing individuality and making it simpler for others to browse through the current patent documents. CPC is a global patent classification scheme that was established in 2012 by the European Patent Office (EPO) and the United States Patent and Trademark Office (USPTO). IPC is a different international categorizing system that was launched in 1971 and is still in use today in 62 nations, although it contains 70,000 codes, which makes it difficult to find information. The CPC offers over 250,000 codes that were constructed with 90% European and 10% US patent classifications, as well as additional classifications based on technological advancements, such as a B section code for Performing Operations and Transporting, whereas B82 subsection for Nanotechnology. [197]. Currently, more than 30 offices throughout the world – including the IP Australia of Australia, the KIPO of Korea, the INPI Brazil of Brazil, the CNIPA (often referred to as SIPO) of China, and others – use the CPC code. These offices include the USPTO of the USA and the EPO of the EU (Figure 8c) [198].

To retrieve the specific patents under NM-based BESS, B82Y, Y02E 60/10, and H01M codes were used. According to the IPC codes assigned to the analyzed patents, Figure 8c depicts the technical subsections of patents registered in this area and the distribution of patent documents across various CPC sub-groups on NM-based BESS. It needs to be pointed out that any patent may have more than one IPC code because each one might be associated with several fields or subfields. According to Figure 8c, the most common Y02E60/10 codes, which account for 69 patents, are related to energy storage using batteries. The following ranks also include the codes H01M10/0525 and B82Y30/00, which are associated with LIBs and nanotechnology for materials or surface science (*e.g.*, nanocomposites), respectively. It is important to point out that due to the potential for multiple areas or sub-fields to be associated with one invention, it is possible for a patent to possess more than one IPC code.

4.7 Top cited patents

References or citations of other patent publications in the same or different technological disciplines are known as patent citations. They are presented as both backward and forward citations. Backward citations are references to patent documents that were published and made publicly accessible before the filing date of the cited patent application. These are additionally known as “prior art.” Ideally, all of the patent information that is publicly accessible prior to the date a patent is filed is referred to as prior art or backward citations. Backward citations also have an impact on the range of a given application's claims. Conversely, forward citations are references to a patent application that has recently been published in a patent document. Therefore, after a patent application is submitted, it can be referenced in publications such as new patent applications, journals, academic papers, *etc*. These would fall under the category of a forward citation. These are considered the class of forward citations [199]. Patent citations are crucial because inventors use them to describe the state of earlier technologies that the current invention builds upon and patent examiners use them to find earlier innovations that may have been overlooked or concealed in the application or to reject it entirely [200].

The technical and commercial strength of a patent can be reasonably extrapolated from the number of forward citations to that patent. The number of patent citations (forward citations) is used to assess the importance of the related technological knowledge domains as a foundation for ensuing technological breakthroughs. Citation data offer the chance to evaluate a patent's technical significance for future advances, with widely cited patents appearing to have higher economic value. Thus, taking into account the number of citations can help determine how directly innovative effort has affected the direction of future knowledge accumulation. The amount of citations that a patent document or patent family achieves is a measure of its social and economic significance; hence, study on citations of patent papers is a major area of interest. Analysis of patent citations can also reveal related patent documents, technology spillovers, and technology trajectories in a specific field of technology [201]. Top-cited patents could be used as an indicator for patents covering basic aspects of technologies as they are able to demonstrate their importance to subsequent advances and, therefore, signify knowledge flows. Figure 8d depicts the number of patent citations under NM-based BESS. It is shown that only 2 out of the 89 patents registered in this technological area have more than 100 citations. The patent titled "Energy storage device" had the highest citation number (105) and was registered under US jurisdiction in 2010. The patent with the next citation number (103) was entitled "Method of depositing silicon on carbon," which was registered in the same jurisdiction in 2012. There were only 3 patents under the group of 40–100 citation numbers. They are titled "Method of depositing silicon on carbon nanomaterials and forming an anode for use in lithium-ion batteries," "Nanotube-based nanomaterial membranes," and "Nanotechnology for electrochemical and energy devices," with citation numbers 91, 64, and 48, respectively. Conversely, 10 patents were found in the citation number range of 20–40. However, 25 patents have not yet been cited. The rest of the patents were in the 1–40 citation range. Therefore, most of the patents cited were under US jurisdiction and subsequently under WIPO.

4.8 Co-inventorship network analysis

Scientific collaborative networks are considered concurrent academic research. Scientific collaboration is the connection between two or more scientists that occurs in the context of society and allows the exchange of meaning and task completion in relation to a common objective. Due to the access to various fields that scientific collaboration provides, it may assist in increasing the scope of research and fostering innovation. Scientists today operate as part of scientific networks collaborating rather than as individual players to find solutions to the technological, social, economic, and political issues that are typically referred to as a multi-disciplinary approach. When researchers work together, they can construct communication networks, share resources, ideas, and information, produce and disseminate novel findings, and eventually produce innovations, which lowers the cost and boosts the output of research. Due to the possibility of discovering novel concepts, the growing specialization within science, the level of complexity of the infrastructure needed, and the requirement of incorporating various types of knowledge, scientists are motivated to collaborate [202,203].

Networks of patent co-inventorship are crucial for information acquisition and have an impact on innovation [204]. The concept of representing co-inventorship networks has been an area of significant interest since the inception of the patent/bibliometric study. Representation of co-inventorship networks has proven to be an effective method for analyzing diverse patent networks, such as networks that show co-inventorship among researchers or inventors. Consequently, there has been a growing interest among researchers, inventors, research institutions, and funding agencies in visualizing co-inventorship networks. The analysis of co-inventorship networks is crucial to make visualizations of these networks accessible to a broader audience, including individuals both within and outside the patent research community. Within co-inventorship networks, researchers are connected to one another depending on the number of inventions they have collaboratively developed [205]. Analysis of the co-inventorship network is performed to visualize the research networks between the different inventors and to determine which inventors have co-inventoried with the highest number of other inventors in the data set [206]. An understanding of the patterns of cooperation among organizations and individuals is provided by co-inventorship analysis in scientific and technology partnerships. An official declaration of the collaboration of two or more individuals or organizations is the co-inventorship of a technical document. Co-inventorship analysis is still commonly applied to understanding and evaluating patterns of scientific collaboration in spite of disagreements over its definition and interpretation [202,207].

Several software tools, including R, Bibexcel, VOSviewer, Publish or Perish, Ucinet, CiteSpace, Pajek, Scholarometer, HistCite, *etc*., are available for data analysis and visualization in relation to co-authorship and co-inventorship. Among these tools, VOSviewer receives special consideration for the visual depiction of bibliometric maps. VOSviewer is a user-friendly computer application that integrates both the VOS mapping approach and an updated viewer that is freely available to the bibliometric research group (see www.vosviewer.com). Consequently, it is particularly effective for easily interpreting larger bibliometric maps. For instance, VOSviewer can be used to create maps of authors or journals based on data from co-citations or create maps of keywords based on data from co-occurrences. A map can be displayed using VOSviewer in a variety of ways, each emphasizing a distinct component of the map [208].

The VOSviewer software generates a co-inventorship network with nodes and edges (links). The nodes can represent various entities, such as inventors, authors, or keywords. The edges represent the connections between pairs of nodes. By default, VOSviewer also automatically assigns the nodes in a network to clusters. A cluster refers to a collection of interconnected nodes that are strongly associated with each other. Every node in a network is allocated to precisely one cluster. An object can only be assigned to a single cluster. VOSviewer utilizes colors to represent the cluster assignment of a node in the viewing of a co-inventorship network [205].

In the present study, a total of 251 inventors contributed to generating the patent documents in NM-based BESS. The software included inventors in the network map who had co-inventored with at least one additional inventor in the data file. In Figure 9a, it is shown that the inventors are organized into different clusters (74 clusters) by the software. The inventors who are grouped together suggest that they are closely tied to one another in terms of their co-inventorship. Among these groups, cluster 1 (Figure 9b) has the most inventors (13), followed by Clusters 2 (Figures 9c) and 3 (Figure 9d) with (11) and (10), respectively. The inventors “Christensen, Gary” and “Luo, Shuji” have co-inventored with the highest number of authors (12) with the greater total link strength in the data file, as seen in Figure 9a, and they are under cluster 1. Both inventors, “Klande, Tobias” and “Engheta, Behrouz,” under the same cluster have co-inventored with 11 authors. Conversely, all authors under cluster 2 have co-inventored with 10 innovators. The generated network map demonstrates a strong commitment to collaboration among innovators in NM-based BESS.

5 Key issues and challenges

Although the advantages of employing NMs in ESSs seem to outweigh their drawbacks, it is crucial to understand the inherent challenges involved in their synthesis and implementation. Here, we briefly outline the challenges and issues that should be addressed during the design, synthesis, and application of NMs for ESVs. Here, we discuss various key issues regarding NM applications in batteries including the large volume changes of NMs during the charge/discharge process, formation of SEI layer, electron or ion transport, atom/molecule diffusion over the charge and discharge event, *etc*. and illustrated in Figure 10.

5.1 Large volume changes of NMs during the charge/discharge process

Due to the huge amounts of Li that are ingested throughout the Li insertion and extraction performance, the nanosized electrode materials typically experience significant volume changes, while conventional electrode materials have a much lower amount of volume changes (<10%). One of the main challenges impeding the use of high-capacity nanostructured electrode materials has been recognized as the significant volume change during the process of charging and discharging. When electrochemical cycling occurs, these large changes in volume cause mechanical degradation in both the active components and electrodes, greatly reducing the cycle life [209]. For example, the Si anode displays very significant volume changes as well as transformations of its structure during the charge and discharge processes. When active particles cycle under such obviously significant volumetric expansion and contraction, they crack, fracture, and pulverize, which results in a disruption of electrical contact (Figure 10a) [211,212]. In addition, major mechanical degradation of the electrode occurs due to the displacement of the particle layers (Figure 10b). The majority of bulk films and big particles eventually experience severe capacity degradation due to this mechanism of particle and electrode fracture, cracking, and pulverization (Figure 10c) [213,214].

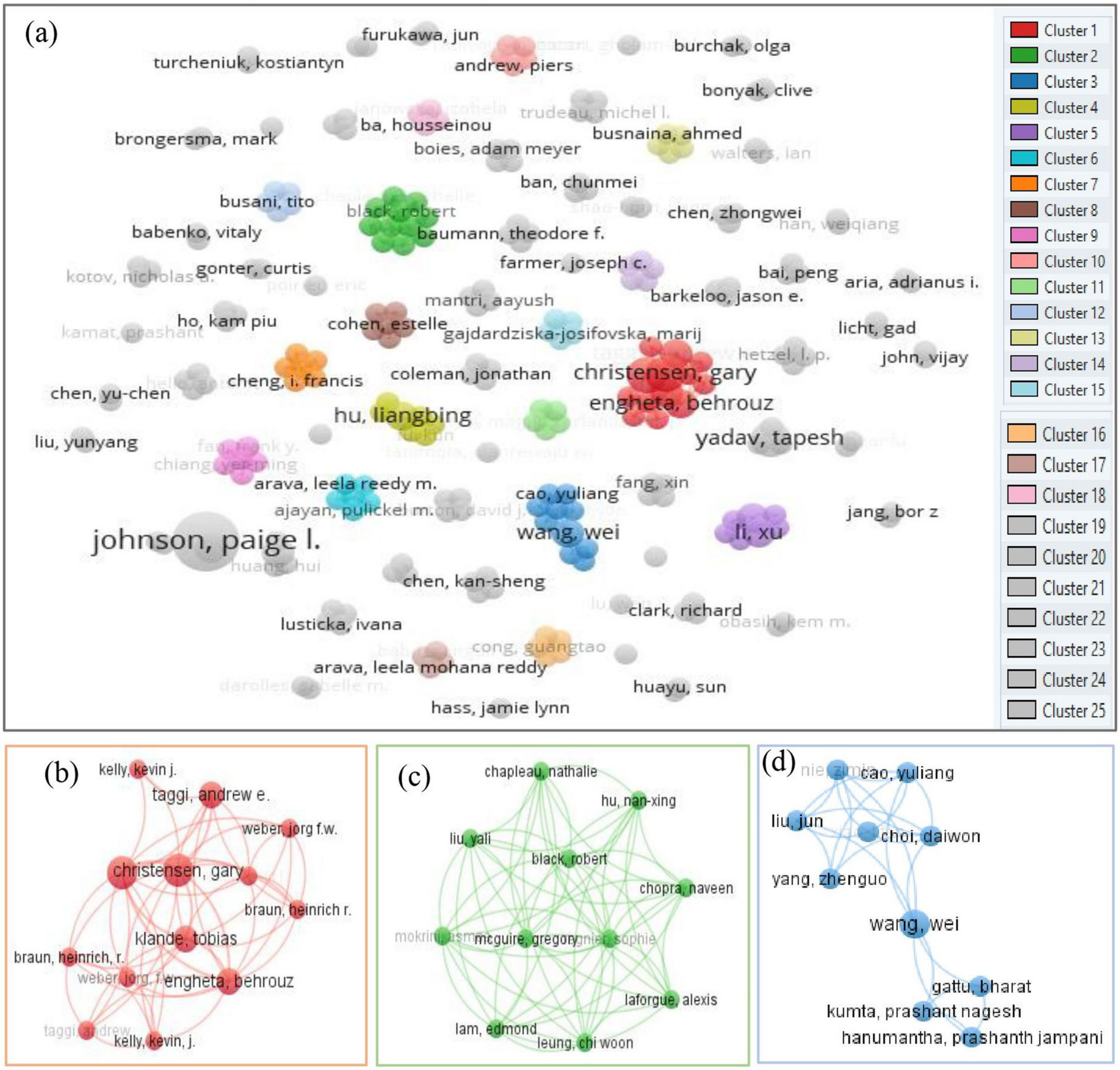


Figure 9: The co-inventorship network map of various inventors conducting research on NM-based BESS based on total link strength. (a) The inventors' co-occurrence network map of all clusters (74 clusters). (b) Co-occurrence map of cluster 1, this group consists of the highest number of inventors (13 inventors). (c) Co-occurrence map of cluster 2, this group consists of 11 inventors. (d) Co-occurrence map of cluster 3, this group consists of 10 inventors. The size of nodes indicates the frequency of occurrence. Their co-occurrence in the same patent is represented by the curves connecting the nodes.

5.2 Stable SEI formation

During the initial charging cycles of LIBs, an electrochemical reduction of the electrolyte results in the formation of an SEI. A passivation layer is provided on the anode surface by the SEI, preventing further electrolyte breakdown and enabling the long battery life needed for many applications (Figure 10d) [210,215]. Although SEI is a Li-ion conductor, it is also an electronic insulator, resulting in the termination of SEI's growth at a certain thickness [215]. Higher CE and a long lifespan of anodes resulting from surface passivation are made possible by a stable SEI layer. A significant movement and change occur on the electrode and electrolyte interface due to the repeated massive volume changes during lithiation and delithiation, which makes it extremely difficult to keep a stable SEI for high-capacity electrode materials [73,209].

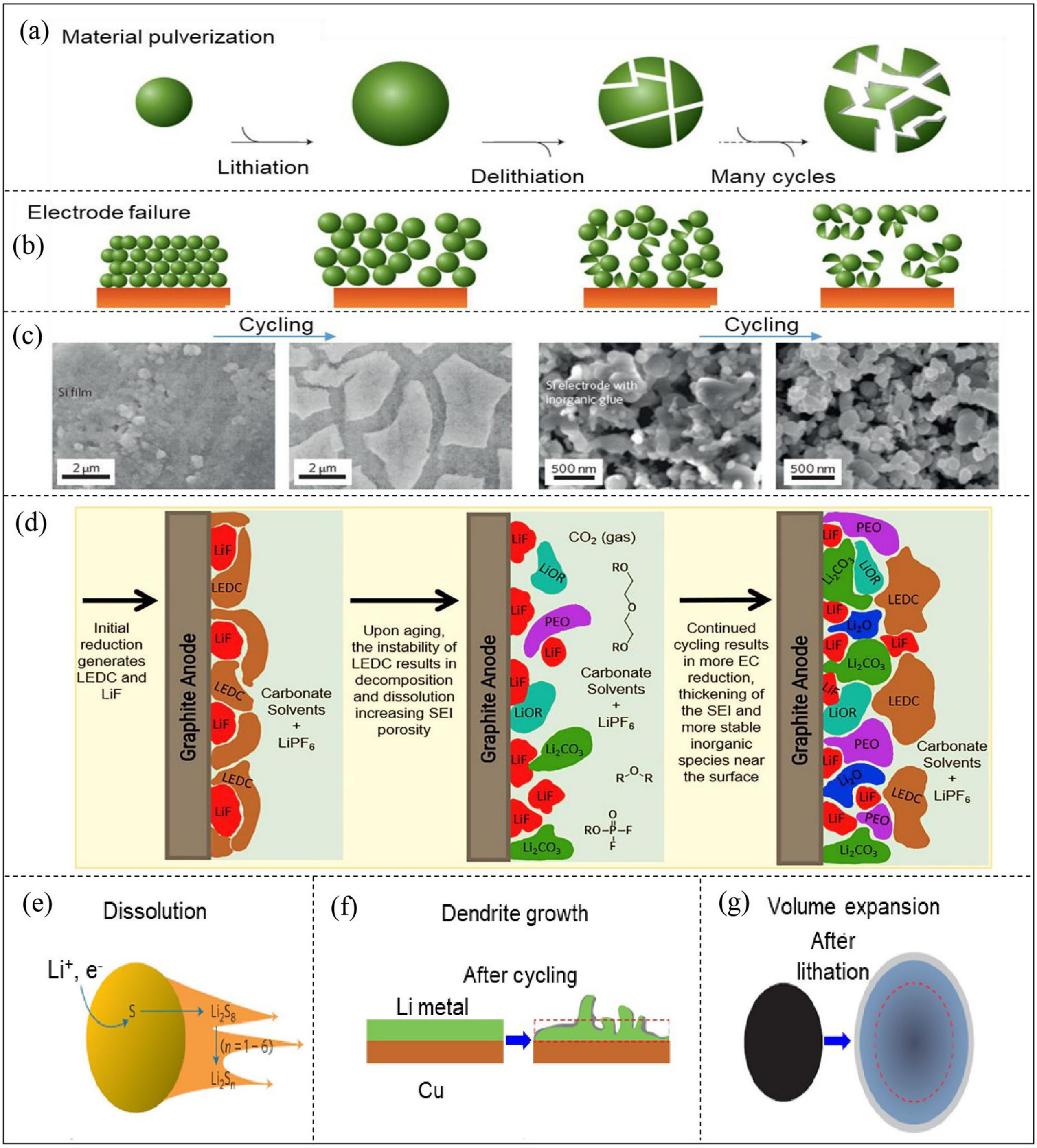


Figure 10: (a)–(c) Diagram of cracking and fracture of high-capacity active particles and electrodes during lithiation and delithiation cycling. The mechanical degradation of high-capacity material at the particle level (a) and electrode level (b) during discharge and charge cycling. (c) SEM images of an Si nanoparticle electrode before (left) and after (right) 20 discharge/charge cycles between 0.9 and 0.01 V at C/10. The Si film electrode cracked like mud in a dry lake bed bottom. The morphology of the Si nanoparticle electrode did not change much due to limited particle and electrode fracture. (d) A schematic showing how the SEI initially formed on the graphite anode, how acid-mediated thermal decomposition reactions affected the SEI's structure, and how further electrolyte reduction caused the SEI to thicken are shown. (e)–(g) Schematic diagram for understanding electrode atom or molecule transportation. (e) Solid–liquid phase transformation: dissolution and diffusion of polysulfide in sulfur cathodes. (f) Formation of lithium dendrite in the anodes of lithium metal. (g) Volume expansion for high-capacity alloy-type electrodes. Reproduced with permission from (a), (b), (c), (e), (f), and (g) Sun *et al.* [209]; (d) Heiskanan *et al.* [210].

5.3 Rapid electron and ion transport

An extensive knowledge of the electrochemical principles underlying batteries will make it easier to develop revolutionary battery technologies that can solve the challenges of powering intensive grid storage and transportation applications. Herein, the understanding of the ion and electron movement is the main issue [216]. Battery performance depends primarily on rapid charge carrier transpiration both throughout the entire electrode and inside individual particles. To attain high rates and activate insulating electrode materials, short distances for ion transport and highly conductive electron pathways can be useful. NMs have considerably smaller dimensions than materials having a micrometer scale. Due to the shorter transport distances compared to those of microparticles, electron transport and Li-ion insertion and extraction within the NPs are greatly enhanced for every single particle [3]. For an electrode to work properly, ions must move through a variety of length scales; this is applicable to both anodes and cathodes. Effective ionic conductivity for porous electrodes is inversely proportional to electrode tortuosity [216].

5.4 Movement of molecules and atoms in long-distance electrodes

During Li insertion and extraction, conventional insertion-type electrode materials do not experience bond breakage and only show slight structure alterations and a small expansion of volume (10%). Therefore, they are stable host materials. Conversely, the structure of high-capacity electrode materials degrades due to extensive bond breakage and entire crystallographic structure alterations. Thus, it has always been thought that their usage in Li-based rechargeable batteries is unfeasible. Due to the significant structural changes, these high-capacity electrode materials have significant difficulties with active atom or molecule diffusion throughout repeatedly occurring charge and discharge cycles, leading to major challenges with battery efficiency. The three types of electrode atom or molecule mobility are as follows: First, phase conversion as well as atom or molecule diffusion, for example, phase conversion of the gas–solid–liquid state in the oxygen cathode of $Li–O_2$ batteries and the solid–liquid state in the sulfur cathode of Li–S batteries (Figure 10e). Second, Li dendrite formation within second-generation Li metal batteries throughout electrochemical Li plating (Figure 10f). Third, the massive amounts of Li consumed result in a significant volume expansion for high-capacity alloy-type electrodes (Figure 10g) [209].

6 Prospects and conclusion

A significant technological challenge for portable devices, electric automobiles, and grid-scale energy storage is the creation of next-generation NM-based rechargeable batteries with lower cost, high energy density, and better safety. Recent advances in nanotechnology over the past decade have provided battery researchers with useful solutions to some of the most significant challenges for subsequent-generation battery chemistries. A summary of the main uses of nanotechnology in batteries includes

- In addition to allowing electron/ion flow within the electrode, decreasing the electrode material sizes can lower the material’s cracking threshold upon lithiation.
- With a range of surface coatings and functionalization layers, electrode materials could be effectively created utilizing nanotechnology, protecting them from harmful interactions in the battery system.
- The ability to engineer all of the components of a battery using nanotechnology allows for the development of novel functionality for batteries that are not possible using conventional approaches.

BESS has advanced significantly over the past decade and is now viewed as a feasible technology with optimization potential for the next smart grids and portable electronic devices. For this reason, academics, researchers, professionals, and decision-makers must have a thorough understanding of the technological knowledge landscape. This study explored and analyzed the NM-based BESS-related PL. This analysis is anticipated to be useful information in the field of energy storage technologies. ESSs will inevitably become increasingly popular as the world moves toward renewable energy sources, which will necessitate a thorough knowledge of every facet of this technology. The principal objective of this PLA was to enhance awareness of the technical competitive advantages of NM-based BESS. A collection of 89 patent files that are relevant to the area of interest after thorough assessment using the Lens database to determine the present condition of grid-connected LIB ESS. Initially, a total of 89 patent files relevant to NM-based BESS were collected through an extensive evaluation using the LENS database to determine the current status. The patent documents based on the area of interest are statistically and technologically analyzed in this study.

PLA was carried out under various parameters based on the scope of the patent documents such as growth of patents, patent families, key players in markets, legal status, classification based on IPC code, top cited patents, *etc*. According to trends in patent publication, the number of patents published overall is rising each year, particularly over the last 10 years (2010–2020), when a significant increase was seen. Patent families are addressed to rapidly identify patents related to a specific innovation as well as simplify the analysis. Hheli LLC (USA-based Company) was the first key player in markets for both owners and applicants, contributing a maximum number of patents. Thus, the United States presently leads the world in patent publication, indicating that it also leads in NM-based BESS. This statement is also supported by the analysis of patent jurisdiction. A total of 56 patents (63%) have been registered under US jurisdiction. Moreover, the majority of the cited patents fell within US jurisdiction. Under the legal status, it was observed that number of pending patents is higher (43.82%) than active patents (29.21%). This is because the patent approval process takes longer to complete due to the complexity of the invention as well as the application backlog at the USPTO. However, there were remarkably few inactive and expired patents, indicating that the research trend in NM-based BESS is increasing. Important findings from the analysis of patent documents and scholarly publications are listed below.

The PLA demonstrates the increasing trend of patents related to NM-based BESS, which is partially reflected in patenting activity. This PLA review focuses on the current nanotechnology-based design concepts to address the challenges confronting future battery chemistries. Strategies like nanostructuring, nanoconfinement, and surface protection have proven to be successful in developing highly efficient energy storage materials. Furthermore, the design of NMs can also have a significant impact on enhancing battery safety, as well as boosting the stability and capacity of large-scale ESSs. For instance, carbonaceous materials continue to be the most prominent electrode materials used in LIBs. In addition, the use of CNT and graphene NMs has increased significantly. Nevertheless, due to the high cost, lack of availability, and technical difficulties of nanocarbonaceous materials, hard and soft carbon are still dominating the market of commercial ESS. The NMs of silicon, tin, aluminum, titanium, and silicon oxide are interesting candidates for electrode materials to develop high-energy-density ESS. Among these NMs, Si and Sn have attracted more attention from researchers compared to Al, Ti, and SiO_2. Si is the only substance whose patenting activity has not decreased recently, even surpassing Sn-based NPs to take second place after carbonaceous NMs. Therefore, NMs of Si are a highly promising element to enhance ESS for researchers and industrialists, and Si has emerged as the leading candidate for large-volume applications. However, only a small percentage of Si is applied in Si/graphitic composite anodes in commercial ESS, indicating that there are still significant challenges to raising the Si content in terms of durability and reliable performance. This is because the percentage increase and accumulation of Si induce significant volume expansion, cycle degradation, and pulverization. This opens up a wide range of possibilities for academia, researchers, and industrialists, with the potential for ground-breaking innovation.

Overall, nanotechnology has a promising future, but more research and studies are needed to expedite the widespread use of NMs in ESS through inexpensive and ecologically acceptable technology. To achieve future progress in NM-based BESS, it is crucial to focus on cost reduction strategies, improve durability through material improvements, scale up manufacturing processes, enhance energy efficiency, and undertake research on novel materials. By resolving these issues, the NM-based BESS can enhance its economic feasibility, reliability, scalability, energy efficiency, and advancements in technology. This would facilitate the wider acceptance and utilization of sustainable energy sources. The notable expansion of NM-based BESS is expected to continue and encourage additional advancements. Therefore, the analysis of the PL in the field of NM-based BESS is comprehensive and critical, as this research field is being expanded by the potential for widespread market deployment. Researchers have been closely monitoring this trend, and they have quickly identified a few primary development options, with Si and carbonaceous NMs taking the highest priority. Researchers paid less attention to other materials, like Al, Ti, Sn, Sb, *etc*., and are also less aware of their commercial application. This demonstrates that the inherent problems of these NMs have not yet been resolved or that there are still challenges to be addressed before applying them commercially as electrode materials to enhance ESS. This might be an opportunity for innovative scientific research to overcome existing issues and challenges as well as open the door to commercialization.

Therefore, the PL of NM-based BESS might offer useful information on potential future development directions. Finally, this article provides some novel viewpoints for potential future study opportunities. Future studies might take into account including more information sources to complement the PLA approach. A more fundamental science-focused knowledge landscape can be mapped out using data from patents and scientific publications. The mentioned finding could be useful for determining potential research gaps between scientists and industrialists.

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