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A Review of Perovskite-based Lithium-Ion Battery Materials

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Abstract. Lithium-ion batteries (Li-ion batteries or LIBs) have garnered significant interest over the past few decades as a promising technology in the energy industry and electronic devices. This is due to their superior energy and power density profiles, compact size, long cycle life, low self-discharge rate, no memory effect, long-lasting power properties, and environmental friendliness. The continuous advancement of electrode and electrolyte materials has greatly enhanced and expanded the application of lithium-ion battery technology. Among the non-precious metal-based materials, perovskites have emerged as noteworthy contenders in the past decade, holding a prominent position in materials science and energy applications due to their unique physical and chemical properties, including exceptional electrochemical stability, high electronic and ionic conductivity, and the ability to be tailored through doping and element substitution. These characteristics make perovskites promising candidates for enhancing the performance of LIBs. This review focuses on the novel application of perovskite materials in LIBs, highlighting their potential to revolutionize the field of energy storage. The review also presents a comprehensive overview of recent advances in perovskite-based LIBs materials, focusing on novel compositions and structures, their properties, and the optimization of fabrication methods. Additionally, it delves into the applications and underlying mechanisms of these materials. By reviewing these advancements, the article aims to highlight the significant potential of perovskite materials in improving the efficiency, durability, and sustainability of lithium-ion batteries, ultimately contributing to the advancement of modern energy storage technologies.

Keywords: Perovskite, lithium-ion battery, energy, electrode, electrolyte.

Classification numbers: 2.2.2, 2.8.3, 4.1.1.

1. INTRODUCTION

Lithium-ion batteries (Li-ion batteries or LIBs) have emerged as the preferred option, effectively dominating the rechargeable batteries market for mobile electronics and hybrid vehicles (HEVs) for over the past few decades. This supremacy is attributed to their superior energy and power density profiles, small size, long cycle life, low self-discharge rate, no memory effect, long-lasting power properties, and environmental friendliness [1 - 5]. Compared to other battery types, such as lead-acid batteries, they offer significant advantages due to exhibiting up to 10-fold densities that make higher energy density than their counterparts, making them more efficient and useful [2]. Notably, lithium batteries possess a crucial advantage in their high reversibility, facilitating the intercalation and de-intercalation of lithium ions during the charging and discharging processes. This reversible intercalation contributes to consistent and cost-effective charging capabilities while underpinning lithium-ion batteries' extended cycle life and overall dependability. The exceptional performance of lithium-ion batteries renders them highly suitable for a diverse range of applications. They find widespread utilization in electric vehicles, micro-scale devices, and large-scale equipment [6, 7].

The two essential components of an electrochemical cell are the electrodes and the electrolyte. The electrodes consist of anodes and cathodes, which serve as conductors of electrical energy in the form of ions. On the other hand, the electrolyte acts as a liquid medium for the movement of ions and provides a buffer to facilitate electrochemical reactions within the battery [8,9]. In practice, the electrochemical properties of the electrodes and electrolytes must be carefully balanced with secondary characteristics such as chemical stability and compatibility with other battery components. It is essential to ensure that the materials used in these components exhibit the desired electrochemical qualities while maintaining compatibility and stability throughout the battery's lifetime [2, 10, 11]. Battery research and development are focused on optimizing these components to enhance lithium-ion batteries' overall performance, safety, and longevity. Continuous advancements in electrode and electrolyte materials contribute to the improvement and widespread adoption of LIB technology [4, 12].

LIBs have garnered significant attention as a promising technology in the energy industry and for electronic devices over the last two decades [13]. However, the widespread adoption of electrochemical technologies is limited by operational issues, high capital costs, and lifetime (durability and stability) issues. These limitations are primarily related to the electrode materials used in electrochemical technologies, constituting a substantial fraction of their composition. One of the key challenges is the high cost of electrode materials, with many relying on expensive platinum group metals such as platinum and palladium. These cost factors hinder the scalability and cost-effectiveness of electrochemical technologies [14,15]. In the fabrication process of lithium-ion batteries, low-humidity environments are employed to prevent the reaction of atmospheric moisture with lithium ions in the electrolyte solution because lithium-ion batteries are highly reactive with air. Single lithium ions can easily react with water (H_2O) to generate elemental hydrogen fluoride (HF) and other undesirable products. Water, therefore, acts as a destructive element in the chemical reaction process within lithium batteries. HF can be detrimental to the battery system as it degrades the crystal structure of the cathode and anode materials. Additionally, HF interferes with forming a solid electrolyte interphase (SEI) on the carbon anode's surface. The anodes and cathodes in lithium-ion batteries are typically made of carbon and lithium oxide materials, while the electrolyte consists of lithium salts dissolved in organic solvents [16, 17]. It is crucial to develop novel energy materials that can address the limitations associated with electrode materials to overcome these challenges [1, 4]. Finding alternative, cost-effective, and more robust materials is essential for advancing the performance and longevity of electrochemical technologies. Current research endeavors are exploring novel electrode materials, enhancing their effectiveness, stability, and endurance, and investigating alternative electrolytes and battery architectures. These advancements are critical for overcoming current limitations and unleashing the full potential of electrochemical energy storage systems.

The commonly employed anode material in LIBs, $Li_4Ti_5O_{12}$, boasts advantages over other commercial anodes, primarily due to its remarkable capacity sustainment rate. Compared to materials like graphite and silica carbon (Si/C) composites, $Li_4Ti_5O_{12}$ exhibits a capacity of 145 mA/hg at 10 ^oC, a value almost equivalent to 170 mA/hg at 0.5 ^oC. This noteworthy capacity retention across varying rates endows $Li_4Ti_5O_{12}$ with superior cyclic speed and overall performance capabilities. Alongside $Li_4Ti_5O_{12}$, early transition metal oxides characterized by octahedrally connected structures can also effectively integrate Li ions into their structure without significant volume fluctuations, thereby ensuring enhanced cyclic speed and performance. An example is $Nb_xW_yO_z$, which demonstrates exceptional anode attributes despite its simplicity. The precursor material $Sr(Ca_{1/3}Nb_{2/3})O_3$, an ABO_3 perovskite featuring octahedrally connected BO_6 corners, is a foundation for this advancement. The selection of this precursor is based on the distinct basicity variations among Sr, Ca, and Nb. The more basic constituents, Sr and Ca, can be selectively removed through acid treatment, leaving the structure essentially intact yet with an altered, more open framework. This structural modification renders the material particularly suitable for use as an anode material in LIBs [18 - 21]. These treatments in anode material development underline the continuous endeavor to identify alternative substances that can enhance lithium-ion batteries' performance, stability, and cycling proficiency. Integrating novel materials like $Li_4Ti_5O_{12}$ and other transition metal oxides can improve the overall effectiveness and reliability of LIBs.

Non-precious metal-based materials, including porous zeolites, metal-organic frameworks, low-energy band gap transitional metal oxides, electro-active carbon-based compounds, and perovskites, have gained significant attention in the last decade as versatile materials for bi-electrocatalysis, photocatalysis, energy storage, and energy conversion applications [2, 22, 23]. In particular, perovskite has emerged as a leading contender due to its exceptional properties and potential for use in electrochemical energy devices. Perovskites exhibit strong light absorption, high crystalline purity, ease of preparation, and excellent charge transport characteristics. These features make them highly photo- and electrochemically active, making them ideal for various electrochemical energy applications. Perovskites also possess increased electrical and ion conductivity, high charge storage capacity, and superior catalytic properties [2]. These attributes contribute to their effectiveness in energy storage and conversion processes. Recent studies have extensively documented the use of perovskites in various energy applications, including batteries, supercapacitors, photovoltaics, photocatalysis, and electrocatalysis [2, 4, 24, 25]. Iqbal *et al*. (2018) reported one notable application of perovskites in inorganic membranes for oxygen enrichment and methane partial oxidation, which can be employed for syngas production. Perovskite-based oxygen transport membranes have also been explored in solid oxide fuel cells (SOFCs) to generate electricity for clean energy production. These developments highlight the versatility of perovskite materials in energy conversion and storage applications [26]. Continued research and development efforts are focused on enhancing perovskite-based energy devices' performance, stability, and scalability, including exploring new compositions and structures, optimizing fabrication processes, and understanding fundamental mechanisms to unlock the full potential of perovskite materials for a wide range of energy applications.

Perovskites have garnered significant attention in recent years due to their unique structural, electronic, and chemical properties. These materials have the general formula ABX_3, where 'X' is an anion and 'A' and 'B' are cations. They are remarkably versatile and can be used in a variety of applications, such as lithium-ion battery electrode materials. In recent times, perovskite materials characterized by the general formula ABO_3 have garnered considerable attention due to their distinctive cubic crystal structure and diverse physical properties that render them suitable for various exciting technologies [25]. Perovskites are often referred to as “chameleon” advanced owing to their remarkable capacity to manifest multiple physical attributes and facilitate the simultaneous transport of ions and electrons [27]. This phenomenon is recognized as mixed ionic-electronic conductivity (MIEC). The structure of perovskite materials, characterized by their straightforward cubic crystal lattice, offers inherent adaptability and manipulation of their properties. This adaptability derives from the flexibility to modify the A or B sites within the perovskite structure, creating new properties and functionalities. Perovskite-based electrodes have been found to considerably improve the performance of the anode and cathode materials in lithium-ion batteries (LIBs). Perovskites give cathodes a strong foundation for lithium intercalation and de-intercalation, which is essential for preserving stability and capacity across a large number of charge-discharge cycles. The Perovskites can provide greater ionic conductivity and structural stability than conventional electrode materials like graphite and lithium cobalt oxide. The most widely used anode material is graphite because of its consistent electrochemical performance and strong electronic conductivity. However, it has a relatively low theoretical capacity (372 mAh/g) and faces safety issues related to lithium plating at high charge rates. Moreover, lithium cobalt oxide ($LiCoO_2$ as cathode) has been widely used due to its high energy density and stable cycle life. However, it suffers from high cost, toxicity, and limited capacity retention at higher charge/discharge rates.

Perovskites' remarkable physical and chemical features make them suitable for a wide range of advanced applications. These materials demonstrate ferroelectricity, piezoelectricity, high-temperature suitability, gigantic magnetoresistance, charge ordering, thermoelectricity, and magnetic transforcing. This versatility has led to extensive studies on transition metal oxides, including molybdate perovskites, and their applications in different fields, including lithium-ion batteries (LIBs). Molybdate perovskites, such as $PbMoO_3$, $CaMoO_3$, $SrMoO_3$, and $BaMoO_3$, with their unique crystal structure and tunable properties, have garnered interest due to offering potential advantages for energy storage and conversion in LIBs [28, 29]. The $SrMoO_3$, in particular, exhibits a cubic perovskite structure and possesses paramagnetism and metallic conductivity. In addition, it displays lower resistivity at room temperature compared to other perovskites, making it an attractive material for various applications. Similarly, compounds derived from $SrMoO_3$, such as $SrFeO_3$, also exhibit outstanding optical and magnetic properties. Doping, the procedure of introducing impurities into the crystal structure, significantly impacts the material properties of perovskites. Using experimental lattice parameters and atomic positions, scientists have analyzed the undoped and magnesium-doped crystal structures of $SrMoO_3$, respectively [30]. These studies shed light on the potential applications of molybdate perovskites, particularly $SrMoO_3$, in various fields. The exceptional properties of these materials make them promising candidates for use in electronics, optoelectronics, catalysis, and other technological advancements. Further research and exploration of molybdate perovskites and their derivatives will contribute to understanding their unique properties and their utilization in a wide range of applications.

Li-O_2 batteries have emerged as mostly promising candidates in energy storage due to their exceptional theoretical specific energy value, which can reach up to 11.425 Wh/kg, making it the highest among known battery systems. In comparison, Li-ion batteries can theoretically store about 5 - 10 times less energy [31]. The Li-O_2 batteries represent alternative energy storage systems featuring high efficiency and outstanding durability. Perovskite oxides have attracted significant interest as catalysts in Li-O_2 batteries primarily because of their exceptional electrochemical stability, strong electronic and ionic conductivity, and the capability to fine-tune their characteristics through doping and the substitution of elements [32, 33]. Perovskite oxides' mixed ionic-electronic conductivity (MIEC) properties contribute to their excellent catalytic activity. For example, studies have shown that $La_{0,4}Sr_{0,6}CoMn_{0,6}$ perovskite oxide exhibits higher electrochemical performance and electrocatalytic activity than $La_{0,4}Sr_{0,6}CoMn_{0,6}$ [34]. These findings highlight the potential of perovskite oxides as catalysts in Li-O_2 batteries.

Even though Li-ion batteries have made significant advancements in energy storage, they still face challenges in providing the energy density required for electric vehicles to match the range of internal combustion engine-powered cars. The specific mass and volume based on lithium and oxygen in Li-O_2 batteries are about ten times and three times higher than conventional Li-ion batteries, respectively. The Li-ion batteries still offer a high mass theoretical energy density. The garnet-type solid Li-ion conductor $Li_7La_3Zr_2O_{12}$ has high room temperature conductivity and electrochemically undergoes proton exchange in water, making it unstable in aqueous electrolyte solutions [35]. The LIBs can provide power to modern electric vehicles. However, current Li-ion batteries have safety issues and a low operating temperature range for optimal performance. Improvements are needed in energy and power density to overcome these issues. The unique properties of perovskites make them attractive for improving energy storage capabilities and overall battery performance. Continued research and development efforts in perovskite oxide catalysts and other perovskite-based materials are expected to enhance the efficiency, durability, and cycling stability of Li-O_2 battery systems. These advancements can potentially lead to energy density and performance improvements, making them more suitable for electric vehicle applications and other energy storage needs. This article aims to provide an overview of recent developments in the application of perovskites as lithium-ion battery materials, including the exploration of novel compositions and structures, optimization of fabrication methods, and a deeper understanding of the fundamental mechanisms that can unveil the potential of perovskite materials.

2. PEROVSKITE STRUCTURE

In rechargeable lithium batteries, most cathode materials exhibit either a hexagonal layered structure or a spinel structure. Cathode materials possessing high ionic and electronic conductivity play a pivotal role in achieving greater energy density. ABO_3-type perovskite materials have been investigated as promising cathode materials due to their favorable properties [25, 36, 37]. Perovskite materials can achieve enhanced stability by adopting a pseudo-tetragonal crystal structure, which falls between the cubic and tetragonal crystal structures, as illustrated in Figure 1 [38]. The Perovskite materials exhibit certain characteristics, such as being hygroscopic and susceptible to decomposition into their constituent components. These materials can exist in three stable structures at different temperatures: orthorhombic, tetragonal, and cubic. The enthalpy of the precursor phase influences the stability of perovskite compounds and can vary among other halide systems and under different conditions. Batteries utilizing mixed halide/inorganic materials with a perovskite structure have garnered significant attention from researchers due to their relatively high electronic and ionic conductivity [39, 40].

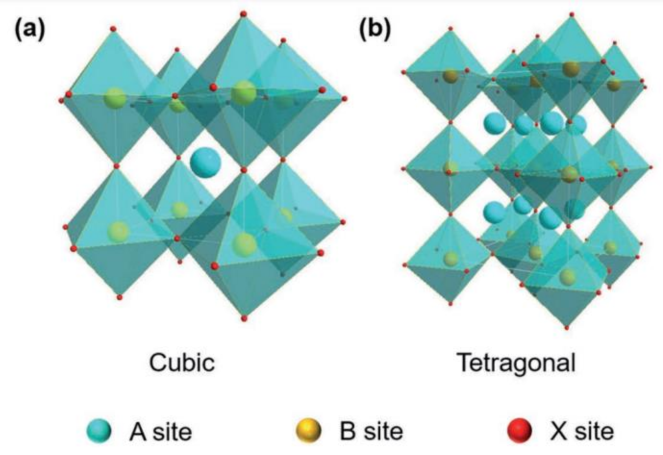

Figure 1. The crystal structure of perovskite materials with different symmetries: a) Cubic, b) Tetragonal. Reproduced with permission from ref. (38), copyright 2017, John Wiley and Sons.

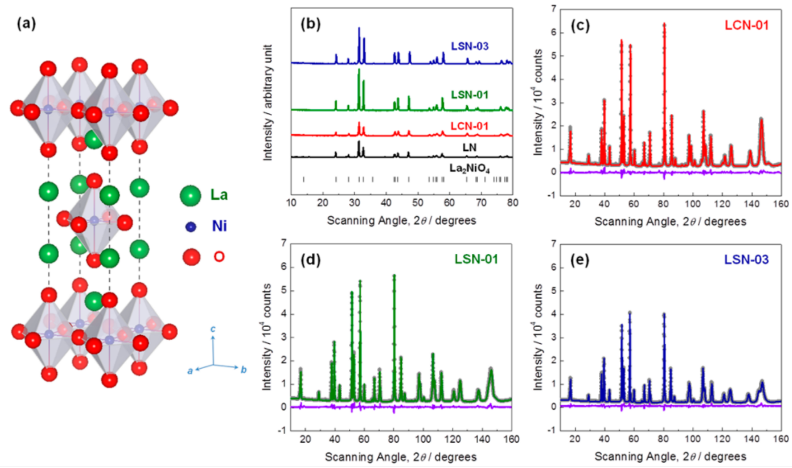

Figure 2. (a) Crystal structure of an La_2NiO_4 layered perovskite; (b) XRD pattern of La_2NiO_4 (LN), $La_{1.9}C_{0.1}NiO_4$ (LCN-01), $La_{1.9}Sr_{0.1}NiO_4$ (LSN-01), and $La_{1.7}Sr_{0.3}NiO_4$ (LSN-03); (c-e) NPD patterns. Reproduced with permission from ref. [45], copyright 2013, American Chemical Society.

ABO_3-based perovskite composite oxides, with their structural and chemical flexibility, are promising multifunctional materials, including catalysts [41, 42]. In these materials, the transition metal element (B cation) occupies the center of an octahedron consisting of six oxygen ions. The B cation can exhibit different valence states within the range of 3 to 6 in perovskite-type oxides [43]. The catalytic properties of perovskite materials make them valuable in developing high-energy storage devices. The surface electronic structure of perovskite materials is a crucial factor in promoting catalytic activity [44].

The structural and catalytic properties of perovskite can be tuned by doping various aliovalent cations onto A_2MO_4. Lanthanum nickelates (La_2NiO_4) were doped with a “layered” perovskite structure that is very active in metal-air batteries. An A_2MO_4 layered perovskite consists of AMO_3 (perovskite) and AO (rock salt) layers along the *c* direction (Figure 2a). Figure 2b displays the X-ray diffraction (XRD) patterns for the untreated or doped La_2NiO_4 catalyst. All XRD patterns are consistent with the data for the layered perovskite structure, which confirms that the partial substitution does not deform the layered characteristics of La_2NiO_4 perovskite nor produces a secondary phase. The neutron powder diffraction patterns (NPD) of the La_2NiO_4 catalyst were collected and analyzed by the Rietveld method to gain a more in-depth understanding of the crystal structure [45].

The ideal perovskite structure is the cubic perovskite structure, as depicted in Figure 3. However, this crystalline structure is susceptible to distortion, resulting in tetragonal, orthorhombic, or rhombohedral variations. These distortions occur due to the substitution or variation of cation A and/or cation B with ions of different valences and sizes. It is possible to fine-tune the properties of perovskite oxides over a broad range by substituting certain cation A and/or cation B ions with other metal ions. This ability to modify their physicochemical characteristics makes perovskite oxides highly versatile and valuable materials in various applications [46]. Cation A substitution in perovskite materials serves the purpose of fine-tuning the oxygen stereochemistry and enhancing the material's conductivity. On the other hand, cation B substitution is utilized to adjust the catalytic activity of the material. These substitutions are crucial for achieving desired properties in perovskite oxides. The ability to modify physicochemical properties such as crystal structure, electrical conductivity, and ionic conductivity makes perovskite oxides ideally adapted for various energy conversion and storage systems. The structure of the electrode materials plays a central role in determining the electrochemical efficacy of these applications. Integrated electrodes comprised of perovskite oxides have been developed to address issues such as carbon and binder instability and boost discharge capacity [47]. This innovation represents a significant advancement in the design of electrodes, including overall performance and stability for energy storage devices.

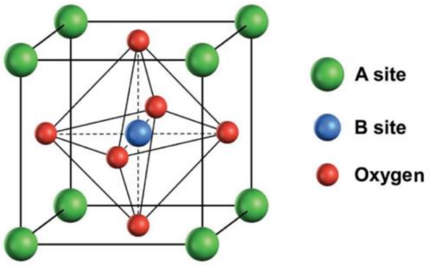

Figure 3. Schematic illustration of an ideal unit cell of perovskite oxide, where A represents a rare-earth or alkaline-earth metal and B denotes a transition metal. Reproduced with permission from ref. [47], copyright 2017, John Wiley and Sons.

3. PEROVSKITE PROPERTIES FOR LITHIUM-ION BATTERY (LIB)

Research on perovskites has primarily centred around their attributes as compounds containing transition metals with d-electrons. Significant research efforts have been devoted in recent years to understanding the structural stability, electronic and optical properties, and electrochemical behaviour of various transition metal oxides (TMOs) concerning their applications in lithium-ion batteries (LIBs). The LIBs have emerged as a compelling, eco-friendly energy source with diverse applications. They are well-suited for applications in portable electronic devices, electric vehicles (EVs), and energy storage systems due to their high energy density, extended cycle life, and portability. The high theoretical capacity of transition metal oxides (TMOs) as anode materials for lithium-ion batteries (LIBs) has prompted extensive research into their potential. Manganese oxide (MnO) has distinguished itself among the examined TMOs due to its encouraging electrochemical performance. The MnO boasts a distinctive structure that facilitates a shorter diffusion path for lithium ions, augmenting its electrochemical properties and contributing to its remarkable effectiveness as an anode material [48]. The LIBs have significantly influenced the landscape of energy storage technology, serving as valuable solutions for storage media, electric vehicles, and electrochemical conversion applications. Their high energy density and enduring cycle life have made them the preferred choice for portable electronic systems and the burgeoning hybrid electric vehicle sector. Nonetheless, the widespread utilization of LIBs in large-scale applications faces limitations related to global lithium resource availability, efficiency, and safety concerns.

The LIBs are well-suited to meet the current demands of electric vehicles (EVs) and power grids due to their high energy density and affordability. However, LIBs have the drawback that, in some circumstances, grid storage is constrained. For instance, adding more battery stacks to electric cars doesn't necessarily address long-distance issues, and the cost factor remains a concern. Nevertheless, LIBs are readily available, and their output can be cost-effectively controlled, making them a viable choice for electricity generation from power plants. As an alternative to lithium-ion technology, Na-ion batteries are cost-effective in efficiency, safety, and long-term sustainability. Transition metal oxides such as $NaTMO_2$ have high energy density and operating voltage. Even cathodes based on materials like $Na(Ni_{0.5}Mn_{0.5})$ demonstrate a specific capacity of 125 mAh/g and high-speed charging capability. Long-cycle stability is challenging for layered oxides due to significant structural changes caused by volume expansion/contraction [48].

Supercapacitors and lithium-ion batteries have high power density, excellent and favourable cyclic performance, fast charge/discharge rate, and safe operation. The advantages of Li-ion batteries include high specification c-capacity fluidity, portability, and high energy density. Based on their charge storage mechanisms, supercapacitors can be categorized into double-layer capacitors and electrical pseudocapacitors. Double-layer capacitors rely on the adsorption and desorption of ions at the electrode/electrolyte interface and often employ conventional carbonaceous materials as electrodes. In contrast, electrical pseudocapacitors involve reversible Faradaic redox reactions occurring over active surface materials, typically using conducting polymers and transition metal oxides/hydroxides as electrodes. Transition metal oxides are well-suited electrode materials for supercapacitors and Li-ion batteries due to their dual-valence properties, environmental friendliness, natural abundance, cost-effectiveness, redox activity, and stable chemical and thermal characteristics. Metal oxide-based perovskite materials, in particular, offer stable structures, a rich presence of oxygen vacancies, and variable oxidation states, making them a subject of extensive research in Li-ion batteries due to their exceptional lithium conductivity and high stability [49].

Perovskite-type oxides have the advantages of low cost and good catalytic performance at low temperatures. ABO_3 perovskite catalysts with high thermal stability, especially lanthanum manganese perovskite oxide ($LaMnO_3$), show excellent catalytic performance for oxidation [50]. Ternary LIBs are commonly used in power tools because of their affordability, substantial discharge capacity, and good thermal stability. These batteries often contain B-site metals, which contribute to their performance. However, it's essential to be aware of the environmental impact associated with Li-ion battery waste. The disposal of LIBs waste has the potential to lead to significant pollution of soil and water sources, highlighting the importance of recycling and proper disposal methods to mitigate these environmental risks [28]. Lithium metal oxide serves as the positive electrode, and carbon serves as the negative electrode in lithium-ion batteries. This substance often takes the form of polyvinylidene (PVDF) or polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP), which serves as a bonding material for a metal current collector [51]. High energy density, high voltage, and long cycle life are all features of lithium-ion batteries. Due to its favourable electrochemical properties, lithium cobalt oxide ($LiCoO_2$) is frequently used as the cathode in Li-ion batteries. However, the cobalt element contained in ($LiCoO_2$) is a heavy metal that is harmful to the environment, has a high cost, is easy to react, and is unstable at high temperatures, making it prone to explosions [52].

4. APPLICATION OF PEROVSKITE FOR LITHIUM BATTERIES

Electrochemical batteries and capacitors have the capability to function as both portable and stationary electric power storage devices. Nanostructured functional materials refer to a class of sophisticated nanotechnology encompassing materials with internal or external dimensions at the nanoscale scale. The compact size of these objects renders them distinctive and holds great potential for implementation in lithium-ion batteries (LIBs). Using nanostructured materials has significant potential in enhancing the electrochemical efficiency of alternative electrodes [53]. Formerly used as an anode material in primary batteries for many years, lithium metal has several limitations in secondary batteries, predominantly due to its reactivity with oxygen and water. There is potential for reintroducing lithium metal as an anode electrode in solid-state batteries. To be incorporated into the active material of the cathode, lithium ions are typically incorporated into the electrolyte of contemporary secondary batteries in the form of lithium compounds. Under controlled charging conditions, lithium migrates from the cathode to the negative anode through the separator electrolyte during the initial phases of formation. The process is reversed during controlled discharge, establishing the solid electrolyte interface (SEI). The described electrochemical process forms an anode material layer in which lithium ions form stable bonds with anode molecules. Due to the loss of lithium and the subsequent formation of a solid electrolyte interphase (SEI) layer, this phenomenon reduces the initial capacitance. In lithium-ion batteries, lithium exists as a cation with a positive charge. During the cycling process, lithium ions undergo a redox reaction in which they migrate from the active material of the anode to the cathode via the electrolyte and reduced separator. As mentioned, the process is distinguished by the repeated passage of lithium ions from the anode to the cathode. Electrostatic attraction between particles of opposite charge is responsible for the continuous migration of lithium cations towards the negative electrode [54].

4.1. Cathode and anode material for battery

Typically, the cathode material utilized in this context is an intercalated compound. Its primary function is to act as a host, facilitating the intercalation and subsequent reversible extraction of Li ions. The LIBs to supply electrical energy per unit mass or volume is determined by the voltage and cell capacity, both of which are significantly influenced by the cathode material. The cathode materials currently used in LIBs have a low energy density and insufficient electronic conductivity, metal oxide material is widely used as cathode for LIBs. Therefore, it is necessary to employ a low-cost solution containing abundant elements to accomplish a battery with a high energy density [53]. Due to their direct effect on the electrochemical efficacy of the battery, the anodes of LIBs are of significant importance. The physical and chemical properties of the anode active material influence the battery's behaviour, requiring careful consideration and regulation. The selection of materials depends on various factors, including but not limited to crystal structure, specific capacity, electrical conductivity, mechanical stability, and intercalation properties. In addition to physical and electrochemical properties, the material's size and shape also affect the LIB's efficacy. There exist two primary concerns about electrode materials: firstly, the necessity to enhance the lithium storage capacity to align with market demands, and secondly, the formidable problem of augmenting cycle stability and speed capability [53]. Currently, porous carbon has been reported in many publications due to their superior electrochemical properties and it is also used in various types of battery, such as alkaline battery, zinc-air battery, and so on.

4.2. Electrochemical mechanism of lithium-ion battery

The movement of lithium ions between the anode and cathode of LIBs generates an electric current via electron flow. When a metal electrode is immersed in an electrolyte, its charge attracts oppositely charged ions, forming a charge layer on the electrode and an “electrical double layer” between the electrodes. This magnetic effect is just one factor influencing lithium-ion movement and current flow [55].

The anode and cathode serve as frameworks for lithium-ion movement. During discharge, ions move from the anode to the cathode, adhering to the cathode's surface. This process, called adsorption or intercalation, involves ions binding to the active material's surface instead of diffusing within it. Electrodes are complex composed of active materials, binders, additives, conductive fillers, and substrates. Researchers fabricate electrodes with large surface areas to minimize energy loss and polarization, especially when the solid electrolyte interphase (SEI) layer forms. Porous electrodes are preferred for enhanced electrolyte penetration and ion propagation [54].

Electrode reactions involve chemical and electrical changes, including metal ion reduction and atom incorporation into the electrode structure. Mass transport, especially in porous electrodes, involves migration (due to electric fields), diffusion (along concentration gradients), and convection (liquid movement). Charging involves cathodic reactions at the anode, releasing electrons through oxidation. Discharge shows cathodic reactions at the cathode, gaining electrons as they move through the circuit from the anode. The anode and cathode roles switch based on operation, affecting voltage conversion. The current direction depends on electrode-initiated oxidation (anode) or reduction (cathode), with lithium ions drawn to the more electronegative electrode, as shown in Figure 4 [54].

The anode undergoes oxidation during charging, losing electrons in a cathodic reaction. Conversely, the cathode experiences an anodic reaction, gaining electrons through reduction. In the discharge phase, this is reverses: the cathode becomes cathodic, receiving electrons as they move through the circuit from the anode. The sequence is shown in Figure 5. If these reactions are fixed, the cell may lose rechargeability after using electrons, becoming inoperable. In an electrochemical cell, as current passes, one electrode becomes anode, the other cathode. However, an electrode's voltage-role connection is not constant. It depends on charge or discharge, affecting voltage conversion. Positive current comes from electrode oxidation (anode), while negative current results from the electrode acting as a cathode, driving reduction. Lithium ions, positively charged, move toward the more electronegative electrode. Their motion is likened to a "*rocking chair*" or "*shuttling*," oscillating between anode and cathode. This analogy portrays lithium-ion back-and-forth movement, resembling a rocking chair's motion. This process is illustrated in Figure 5, capturing the lithium-ion movement's essence [54].

4.3. Perovskite as lithium-ion battery material

Perovskite is a promising material for LIBs applications, due to its superior electrochemical properties and ionic transport mechanism. Previous studies widely used perovskite-based metal oxides and perovskite halides in the battery field. Perovskite, also called as a chameleon material due to the element from ABO_3 or ABX_3 structure, can easily be modified from various sources, depending on the researchers' purposes.

Lian *et al*. employed electrospinning techniques to fabricate composite fibre-based membranes consisting of lithium lanthanum titanate oxide (LLTO) and polyacrylonitrile (PAN) to develop rechargeable lithium-ion batteries (LIBs). The incorporation of LLTO content resulted in a reduction in the average fibre diameter of LLTO/PAN fibres. The outcome is observed after incorporating LLTO particles at a weight percentage of 15 %. When immersed in a liquid electrolyte, the membrane composed of LLTO/PAN composite fibres exhibited favourable compatibility with lithium electrodes. On the other hand, perovskite is also called as a mixed ionic electronic conductivity (MIEC) material, which can transport ions and electrons simultaneously. This favors the utilization of perovskite as a membrane separator in battery applications. Furthermore, it was observed that cells using LLTO/PAN composite fibre-based electrospun membranes, which were immersed in a liquid electrolyte, had an initial discharge capacity of 166 mAh/g and demonstrated consistent cycling performance at a rate of 0.2 ^{o}C. The device has shown a significant volumetric discharge capacity of 2200 mAh cm^{-3}, as reported in reference [56].

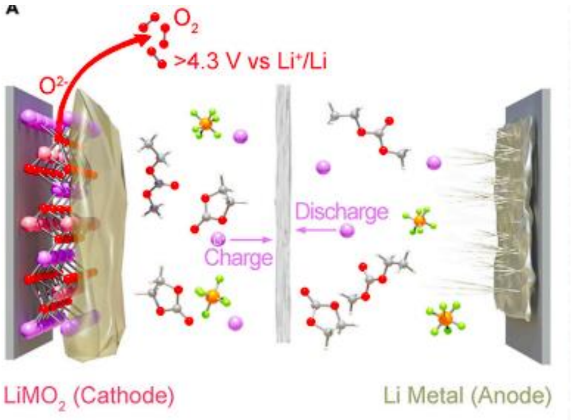

Figure 4. Schematic illustration of LIBs. Reproduced with permission from ref. [54], copyright 2021, Elsevier.

Xia *et al*. [57] conducted research using perovskite as a material for lithium-ion batteries (LIB). Figure 5a displays the initial charge-discharge curves of the synthesized perovskite materials $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ when subjected to a consistent current density of 200 mA/g. The initial discharge capacity of $CH_3NH_3PbI_3$ is 43.6 mAh/g**,** similar to other organic-inorganic hydrides exhibiting values below 50 mAh/g. The initial discharge capacity of $CH_3NH_3PbBr_3$ is significantly higher at 331.8 mAh/g compared to $CH_3NH_3PbI_3$. The precise cause for the enhanced performance of $CH_3NH_3PbBr_3$ remains unclear. However, the lower molecular weight of $CH_3NH_3PbBr_3$ and the higher first charge efficiency observed in Figure 6a suggest that oxidation or reduction reactions at an optimal voltage may be notable. This phenomenon could also be linked to the peak of oxidation or reduction reactions observed in the cyclic voltammetry curve depicted in Figure 5b. Figure 5c provides a comparison of the cycling performance of the two compounds.

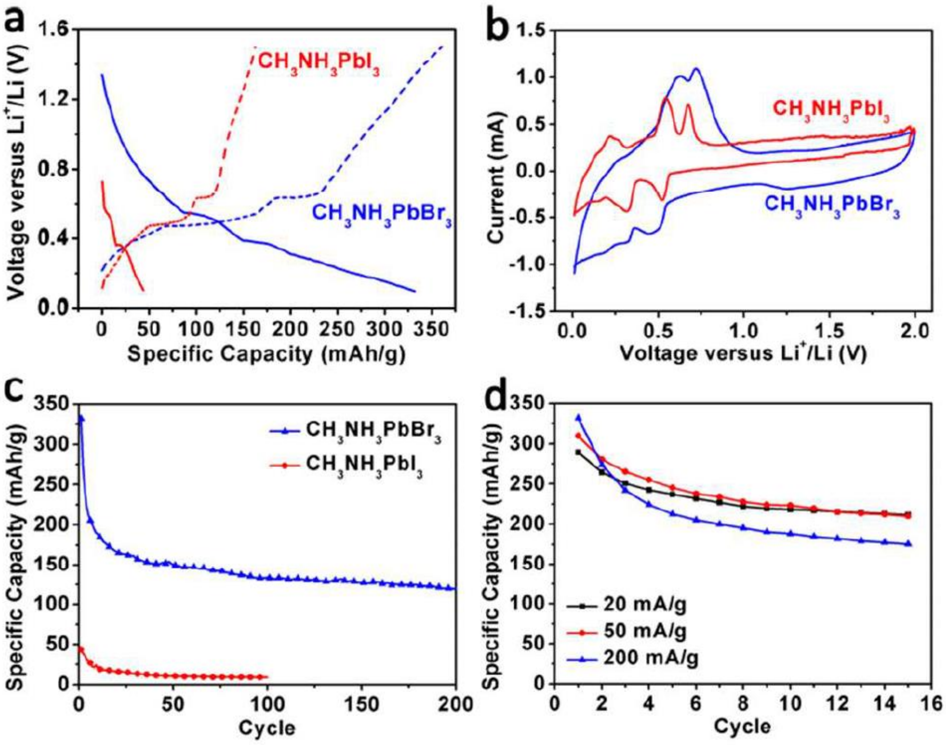

Figure 5. Electrochemical characterizations of Li-ion batteries composed of perovskites $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$: (a) charge-discharge profiles; (b) cyclic voltammetric cures; (c) cycle performance; (d) rate performance of perovskite $CH_3NH_3PbBr_3$. Reproduced with permission from ref. [57], copyright 2015, Royal Society of Chemistry.

The two capabilities exhibit a substantial decrease within the initial 30 cycles, followed by a gradual decline. The potential for enhancing performance in Li-ion battery applications exists because of the structural variety observed in the organometal halide structure of AMX_3 perovskite, where A represents an organic ammonium cation, M denotes a metal cation, and X signifies a halide anion. The rate performance, determined by the cycling performance at various charge-discharge current densities, was also evaluated. The outcomes of this assessment are presented in Figure 6d. In the initial 15 cycles, the discharge capacity exceeds 210 mAh/g when the test current is either 20 mAh/g or 50 mA/g. When subjected to a current density above 200 mAh/g during the charging or discharging process, the discharge capacity of the 15 remains at 175.5 mAh/g, which is comparable to the theoretical capacity of the commercially available $Li_4Ti_6O_{12}$ (175 mAh/g). The favorable rate performance of $CH_3NH_3PbBr_3$ demonstrates its ability to undergo charging and discharging processes at varying rates while maintaining a relatively high capacity. This suggests that the material possesses structural stability, making it suitable for Li-ion batteries [57].

4.4. Application of perovskite as Li-O_2 battery material

The slow accumulation of insoluble discharge and isolated products on the O_2 electrode can potentially obstruct the paths of electrolytes, oxygen, and electrons. This obstruction limits the Li-O_2 battery's rate, capacity, and cycle life. As a significant class of functional inorganic materials, perovskite-based oxides exhibit numerous advantageous physical and chemical properties. These benefits include increased electronic and ionic conductivity, remarkable electrochemical stability, and remarkable catalytic properties. Perovskite-based oxides, therefore, hold promise as electrocatalysts LIBs.

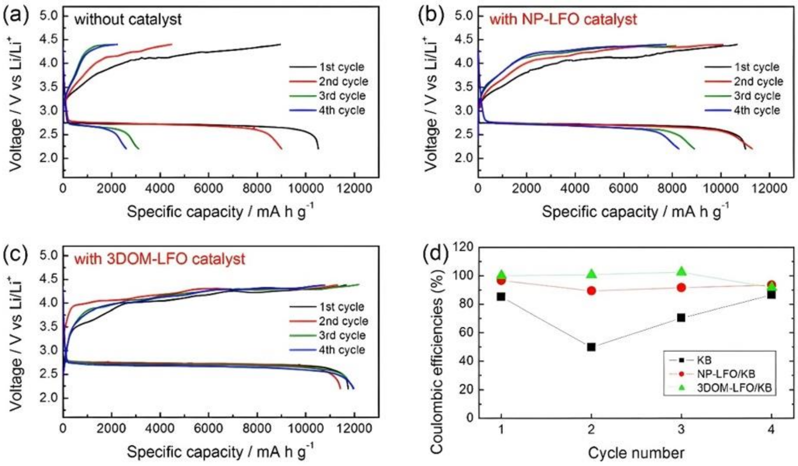

Figure 6. The cyclic performance of lithium-oxygen (Li-O_2) cells was investigated using three different types of electrodes: (a) pure KB; (b) NP-LFO/KB; (c) 3DOM-LFO/KB electrodes at a current density of 0.025 mA cm^{-2}; (d) Comparison of coloumbic efficiency of Li-O_2 cells with three electrode types. Reproduced with permission from ref. [32], copyright 2014, Royal Society of Chemistry.

Xu *et al*. [57] presented a methodical and uncomplicated strategy for synthesizing three-dimensionally organized macroporous $LaFeO_3$ (3DOM-LFO). In the study, O_2 was used as the catalyst electrode, and the Li-O_2 cells demonstrated enhanced speciation, capacity, rate capability, and cycle stability. Brunauer Emmett Teller (BET) measurements revealed that the produced 3DOM-LFO had a surface area of 29.3 m^2 g^{-1}. The organized pore structure of three-dimensionally ordered macroporous lithium ferrite (3DOM-LFO) permits efficient utilization of oxygen and electrolyte within the oxygen electrode, thereby promoting the presence of numerous catalytic active sites and enhancing the electrochemical performance of lithium-oxygen (Li-O_2) batteries. It has been discovered that using a 3DOM-LFO catalyst increases the discharge and charge voltage of Li-O_2 cells, resulting in increased efficiency during the cycling process. When comparing the discharge voltage of a Li-O_2 cell with a 3DOM-LFO/KB electrode to that of an NP-LFO/KB electrode and a KB electrode, the 3DOM-LFO/KB electrode is only marginally superior by approximately 20 mV and about 30 mV, respectively. The charge voltage of the Li-O_2 cell with the 3DOM-LFO/KB electrode is significantly lower than that of the Li-O_2 cell with the NP-LFO/KB electrode and the KB electrode by 150 mV and 250 mV, respectively. The effectiveness of the 3DOM-LOF electrocatalyst in mitigating overpotential in relation to the operational performance of Li-O_2 cells was further investigated. In the range of examined current densities (0.025 to 0.2 mA cm^2), the discharge and retention capacities of Li-O_2 cells with 3DOM-LFO/KB electrodes are superior to those with pure KB electrodes and NP-LFO/KB, as shown in Figures 7a and 7b, respectively. The observed increase in reaction rate may result from the interaction between the catalytic activity energy and the porosity of the 3DOM-LFO catalyst [32].

The cycling of Li-O_2 cells was further examined with three types of O_2 electrodes, as shown in Figure 6d. The Li-O_2 cells, including a three-dimensionally ordered macroporous (3DOM) $LaFeO_3$ (LFO) catalyst, exhibited superior cycle stability compared to cells utilizing non-porous (NP) LFO and pure potassium borate (KB) catalysts. The Li-O_2 cell operating 3DOM-LFO exhibited an initial discharge capacity of 11738 mAh/g, and subsequent cycles maintained a high capacity of 11932 mAh/g, as depicted in Figure 6. In contrast, when using only the KB electrode, there was a significant decline in discharge capacity as the cycling progressed, ultimately reaching a value of 2,571 mAh/g. The enhanced stability of the four-cycle can be ascribed to the distinctive characteristics of the O_2 electrode coupled with the highly structured porous 3DOM-LFO electrocatalyst. The combination enables the production and composition of products, thereby enhancing the O_2 electrode's rechargeability. The literature suggests that the surface discharge of the KB electrode is predominantly adhesive, causing potential obstacles to the transfer of lithium ions and charge within the electrode in subsequent cycles [32].

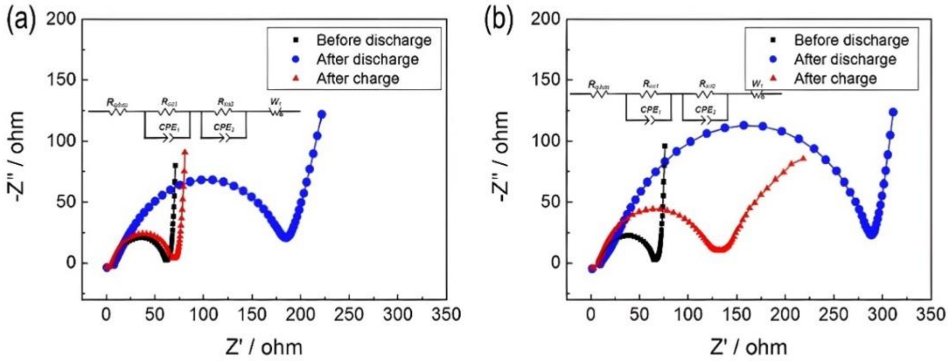

Figure 7. The electrochemical impedance spectra (EIS) of lithium-oxygen (Li-O_2) cells were measured under two conditions: (a) in the presence of a 3DOM lanthanum ferrite (LFO) catalyst and (b) without the catalyst. The measurements were conducted at various discharge/charge stages, with a constant current density of 0.05 mA cm^{-2}. Reproduced with permission from ref. [32], copyright 2014, Royal Society of Chemistry.

According to the data presented in Figure 7, it can be observed that the impedance of both Li-O_2 cells before the initial discharge exhibits a similar trend. During the initial discharge, there was a notable rise in the impedance of both cells, primarily attributed to suboptimal electrical performance. This impedance increase resulted in the formation of conductive discharge products, specifically Li_2O_2, at the O_2 electrode [32].

Kalubarme *et al*. [14] investigated the catalytic potential of $LaNi_xCo_{1-x}O_{3-\delta}$ perovskite in the context of non-aqueous lithium-oxygen batteries. Oxygen electrodes are essential for developing lithium-oxygen batteries because they serve as sites for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The efficacy of oxygen electrodes is significantly influenced by the structure and activity of the materials used to construct them. Electrodes incorporating perovskite oxide catalysts supported by carbon and containing oxygen vacancies exhibit less polarization and a greater discharge capacity than electrodes containing carbon vacancies without catalysts. The $LaNi_{0.25}Co_{0.75}O_{3-\delta}$ catalyst demonstrated superior catalytic performance in the oxygen evolution reaction (OER) by facilitating the oxidation of Li_2O_2 at 3.8 V. The acquired results for perovskite catalysts on lithium-ion batteries (LIBs) have led to the proposal of a mechanism, as seen in Figure 9, that explains the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) processes occurring on the catalyst surface during draining and charging, respectively. During the oxygen reduction reaction (ORR), the supplied oxygen diffuses into the gas diffusion layer and dissolves in the electrolyte. As depicted in Figure 9a, the initial stage of the oxygen reduction reaction (ORR) involves the augmentation of dissolved oxygen through the creation of oxygen vacancies on the surface of the catalyst, followed by the reduction of molecular oxygen (O_2) via electron acceptance, which results in the formation of superoxide ions (O_2). The superoxide species, which has a weak binding affinity, reacts with dissolved Li ions to produce LiO_2. It is essential to remember that LiO_2 is an unstable mediator in the oxygen reduction reaction (ORR) mechanism. The LiO_2 compound, which is unstable, endures a disproportionation process, resulting in the formation of stable Li_2O_2 on its surface [14].

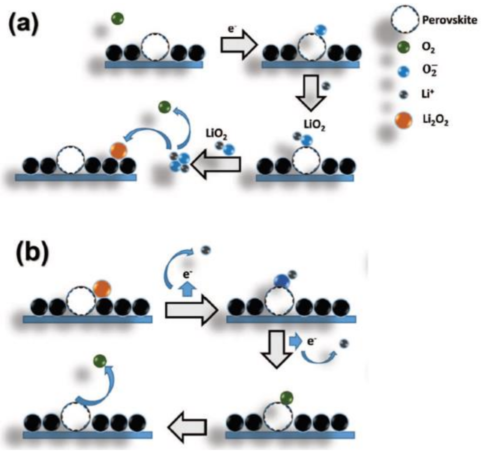

Figure 8. Plausible mechanisms for the (a) ORR and (b) OER processes taking place on the surface of a perovskite catalyst during the discharging and charging stages of a lithium-oxygen (Li-O_2) battery. Reproduced with permission from ref. [14], copyright 2014, IOP Publishing.

The performance of lithium-air batteries is predominantly determined by the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) electrocatalysts. Lu *et al.* [38] utilized highly active $La_{0.8}Sr_{0.2}MnO_3$ (LSM) perovskite nanorods as electrolyzers in their investigation. These nanorods were synthesized and designed specifically for use in lithium-air batteries via soft templates. The LSM nanorods have a microporous structure with numerous defects and a significant surface area. During the discharge and charge processes, these properties can be effectively utilized in the context of ORR and OER. In the context of lithium-air batteries, an investigation was conducted to evaluate the electrocatalytic performance of LSM nanorods, a catalyst with microporous properties. In addition, standard LSM particle catalysts and pure acetylene black electrodes were used for comparison. In their investigation, the catalytic activities of microporous LSM nanorods in terms of oxygen reduction reaction (ORR) and OER were determined using cyclic voltammetry (CV). As depicted in Figure 9a, the experiments were conducted in a TEGDME LiTFSI electrolyte. The examined potential range was from 4.5 to 2.0 V. Comparing the electrodes based on LSM particles and pure acetylene black, it was discovered that the microporous LSM nanorods-based electrode exhibited a greater onset potential (2.86 V) for ORR and a greater peak current ratio of ORR to OER The improved kinetics of ORR and OER are advantageous for enhancing lithium-air batteries' energy dissipation, recharging properties, and cycle life. Figure 9b depicts lithium-air batteries' initial discharge and charge current density profiles with three distinct air electrode catalysts at a current density of 200 mA g^{-1}. At the same time, an initial discharge capacity of 6890 mA g^{-1} is observed for the air lithium battery, employing microporous LSM nanorods as the electrode material. The reported electrode current densities for conventional LSM nanorods and lithium-air batteries based on pure acetylene black are 3,925 and 1,977 mA g^{-1}, respectively [31].

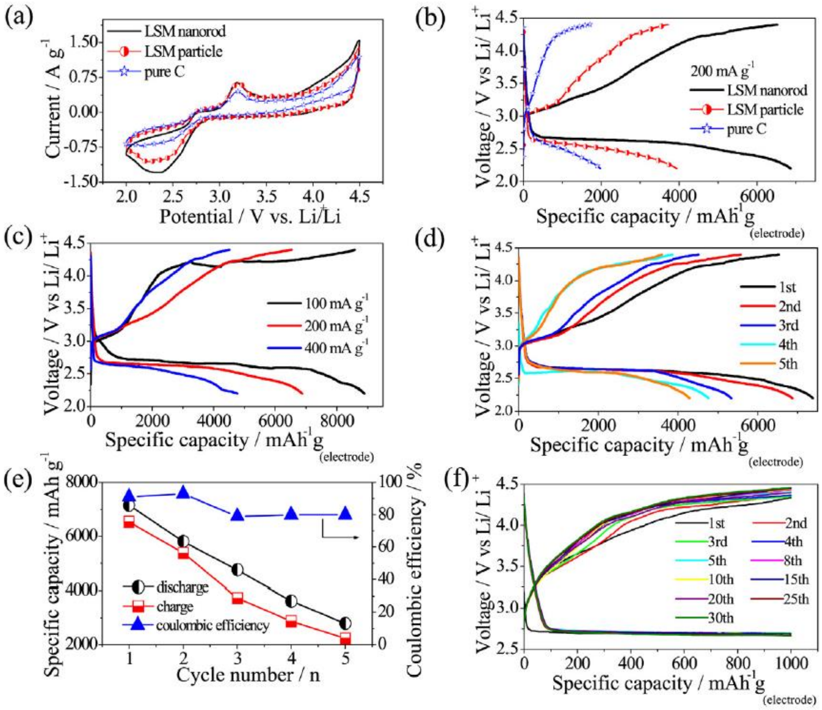

Figure 9. (a) CV curves of microporous LSM nanorods, LSM particles, and pure acetylene black-based lithium-air batteries were obtained at a scan rate of 0.2 mV s^{-1}; (b) A comparison was made between the first discharge-charge curves of different lithium-air batteries at a current density of 200 mA g^{-1}; (c) The rate capacities of lithium-air batteries, utilizing microporous LSM nanorods as a catalyst, were evaluated under various current densities; (d) Typical discharge-charge voltage profiles were observed for the lithium-air batteries; (e) The cycling performance of microporous LSM nanorods catalyst-based lithium-air batteries was assessed during the initial five cycles at a current density of 200 mA g^{-1}, with the voltage range from 2.0 to 4.4 V; (f) The cycling stability of the micro LSM nanorods-based lithium-air battery was investigated under a specific capacity limit of 1000 mAh/g at a current density of 200 mA g^{-1}. Reproduced with permission from ref. [31], copyright 2015, Elsevier.

Figure 9c presents the discharge and charge profiles of the first cycle microporous LSM nanorods lithium-air battery at various current densities (100, 200, and 400 mA g^{-1}) to investigate the speed capabilities. When the current density is reduced from 400 to 100, there is an observed rise in discharge capacity from 4763 to 8890. The voltage difference between high charge and discharge diminishes, suggesting a favourable rate capability. One of the most crucial factors in nonaqueous lithium-air batteries is the stability of discharge and charge. However, the observed behaviour often deviates from this ideal scenario due to factors such as the build-up of discharge byproducts and the stability of the electrolyte. The LSM nanorods microporous lithium-water battery demonstrates consistent cycling performance for five cycles under discharge and 200 mA g^{-1} charge settings, as depicted in Figure 9d. The specific capacity exhibits a retention rate of merely 31 % following five cycles. Additionally, the calculation and depiction of the efficient columbic effect of microporous LSM nanorods lithium-air battery can be observed in Figure 9e, based on the data and charging process illustrated in Figure 9d [31].

A study using organic-inorganic halide perovskite for lithium intercalation and conversion was conducted by Dawson *et al*. The findings of the simulations indicate that the predominant conversion pathway involves the formation of lithium halide (LiX) and lead (Pb) metal, particularly in the cases of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$. The findings were corroborated using electrochemical and powder X-ray diffraction (PXRD) investigations. The results provide a rationalization for the suboptimal electrochemical performance observed in $CH_3NH_3PbI_3$ and shed insight on potential factors contributing to the observed variations among the three hybrid perovskite materials under investigation. In this research, the scientists conducted simulations to examine four main Li concentrations: x = 0.037, 0.125, 0.5, and 1.0 $LixCH_3NH_3PbX_3$. It is important to note that in this context, x = 1.0 signifies full Li intercalation. Li was introduced into octahedral and tetrahedral sites to determine the most stable intercalation site, as depicted in Figure 12 [58]. Table 1 presents the intercalation stresses calculated for each material's octahedral and tetrahedral sites, considering the lowest energy Li-coupled configurations at various concentrations [58].

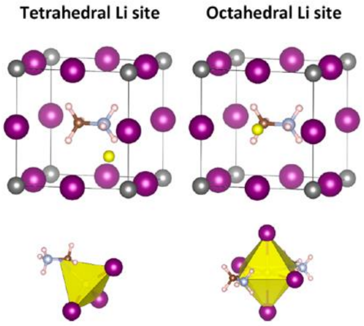

Figure 10. Cubic perovskite structures of $CH_3NH_3PbI_3$ illustrate the presence of two principal Li intercalation sites. The center A-site is occupied by the methylammonium cation ($CH_3NH_3^+$), surrounded by 12 halide ions (purple) that serve as its nearest neighbours. Pb ions are grey. Yellow spheres represent Li intercalation sites in tetrahedral and octahedral structures. In addition, the local coordination environments of the Li^+ ions are shown. Reproduced with permission from ref. [58], copyright 2017, American Chemical Society.

Table 1. The intercalation voltages (V) for the octahedral (Oct) and tetrahedral (Tet) sites with the lowest energy in $LixCH_3NH_3PbX_3$ (where X = I, Br or Cl) are being considered [58].

System	*x*Li = 0.037		*x*Li = 0.125		*x*Li = 0.5		*x*Li = 1.0*	
	Oct	Tet	Oct	Tet	Oct	Tet	Oct	Tet
$CH_3NH_3PbI_3$	1.44	1.40	1.36	1.43	0.25	0.20	0.13	0.00
$CH_3NH_3PbBr_3$	0.57	0.84	0.45	0.81	0.12	0.16	SR	SR
$CH_3NH_3PbCl_3$	0.31	0.59	0.27	0.52	0.18	0.16	SR	SR

The results provided in Table 1 exhibit three primary characteristics. First, the voltage obtained for the electrochemical process observed at the Li$x$$CH_3NH_3PbBr_3$ anode, with a Li concentration of 0.125, falls within the range of 0.5 to 0.7 V. The material properties and lithium content significantly influence the selection of a certain size and the intercorrelation voltage. Second, while considering low concentrations of Li, it is seen that $CH_3NH_3PbI_3$ exhibits a higher preference for Li incorporation compared to other perovskite materials. The diminished distortion of the PbI_6 octahedral in the bigger unit cell of $CH_3NH_3PbI_3$ might be attributed to the increased distance between Pb-Li atoms, which surpasses that of the corresponding octahedral structures in $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$. Third, with complete Li intercalation ($x = 1.0$), the octahedral PbX6 undergoes structural distortion in all three materials, with $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$ exhibiting the most excellent structural distortion. The alteration of the unit cell's configuration throughout optimization, suggests the potential occurrence of conversion or breakdown reactions as the material is almost fully Li-intercalated. The octahedral structure exhibits significant deformation, leading to substantial separations between intercalated Li^+ ions and organic cations [58].

The research focused on the electrochemical behaviour of $CH_3NH_3PbBr_3$, a representative system displaying the highest discharge capacity, wherein Li intercalation or conversion is the dominant process. Electrochemical characterization was performed on this $CH_3NH_3PbBr_3$ perovskite electrode. The cell's open circuit voltage was brought down to 0.1 V at a current density of 20 mA g^{-1} during the initial discharge process. As a result, a specific discharge capacity of 134.3 mAh/g was achieved, corresponding to the intercalation or conversion of 2.4 Li^+ ions per mole of $CH_3NH_3PbBr_3$. Interestingly, the amount of charge transferred during the initial discharge process also accounted for 2.4 Li^+ ions per mole of $CH_3NH_3PbBr_3$. This goes beyond the limit of one vacant site per mole available under the specific conditions in pure $CH_3NH_3PbBr_3$ that is required for the intercalation mechanism to occur. Furthermore, the observed capacity below 1 V might also result from the contribution of electrolyte interactions with the electrode's solid electrolyte interphase (SEI) layer [58].

5. CONCLUSIONS

Several studies have indicated that perovskite materials hold significant potential in lithium-ion battery (LIB) applications due to their remarkable reversibility properties concerning the intercalation and de-intercalation of lithium ions during charge and discharge cycles. Every electrochemical cell consists of two essential components: electrodes and electrolytes. Electrodes encompass anodes and cathodes, serving as conduits for electrical energy in the form of ions. Meanwhile, electrolytes provide a liquid medium for ion migration and act as a buffer to facilitate electrochemical reactions within the battery. The pursuit of perovskite synthesis remains a continuous endeavor, particularly in energy-related fields. Characterization tests utilizing techniques such as SEM, XRD, FTIR, BET, and EDS analysis contribute to understanding perovskite properties. Perovskite materials exhibit heightened energy and power densities, which drive the exploration of new conversion electrode materials. Their capability to circumvent capacity limitations is facilitated by intricate interactions with cation compounds, allowing high capacities to be achieved through the total electrochemical redox process of transition metals. Battery performance hinges on the process of conductive electron transfer. Electron movement occurs from the negative electrode (anode) to the positive electrode (cathode), culminating in generating an electric current and establishing a potential difference.

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Declaration of competing interest. The authors declare that there is no conflict of interest in this article.

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