

A Review: Structure and Synthesis of Perovskite as Lithium-Ion Battery (LIB) Material

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Kata kunci

Baterai Lithium-ion, Perovskit, Bahan elektroda Struktur perovskite, Sintesis Perovskit

Abstrak

Baterai lithium-ion (baterai Li-ion atau LIB) telah mendapatkan perhatian yang signifikan sebagai sumber daya yang sangat menjanjikan. Baterai ini menawarkan profil kepadatan energi dan daya yang sangat baik, bersama dengan sifat-sifat lain yang diinginkan, seperti tidak ada efek memori dan kemampuan daya yang tahan lama. Hal ini membuat teknologi baterai Li-ion sangat dicari dalam industri energi dan perangkat elektronik. Bahan perovskit merupakan salah satu bahan berbasis logam non-mulia yang telah menarik banyak minat dari para peneliti dalam beberapa dekade terakhir. Perovskit sangat menarik karena sifatnya yang luar biasa dan potensi aplikasinya dalam perangkat energi elektrokimia. Perovskit memiliki sifat fisik dan kimia yang sangat baik sehingga sesuai untuk digunakan sebagai bahan elektroda pada baterai lithium-ion yang dapat diisi ulang.

Keywords

Lithium-ion Battery, Perovskite, Electrode materials, Perovskite structure, Perovskite synthesis

Abstract

Lithium-ion battery (Li-ion battery or LIB) has gained significant attention as a highly promising power source. It offers excellent energy and power density profiles, along with other desirable properties such as no memory effect and long-lasting power capabilities. This has made Li-ion battery technology highly sought after in the energy industry and electronic devices. Perovskite materials have emerged as one of the non-precious metal-based materials that have attracted considerable interest in recent decades. Perovskites are highly regarded due to their remarkable properties and their potential applications in electrochemical energy devices. They possess excellent physical and chemical characteristics that make them suitable for use as electrode materials in rechargeable lithium-ion batteries.

Sejarah Artikel

Diterima : 26/07/2023

Disetujui : 22/07/2023

Dipublikasi : 25/07/2023

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INTRODUCTION

Lithium-ion batteries are known for their excellent energy and power density profiles, no memory effect, and long-lasting power properties. They exhibit high reversibility, allowing for efficient intercalation and de-intercalation of lithium ions during the charging and discharging processes [1]–[3]. These batteries consist of two key components: electrodes and electrolytes. The electrodes consist of anodes, and cathodes serve as conductors of electrical energy (ions). The anode and cathode materials facilitate the movement of lithium ions back and forth between them during battery operation. The electrolyte, on the other hand, acts as a liquid medium through which ions can move, facilitating the necessary electrochemical reactions within the battery [4].

Over the past two decades, lithium-ion battery technology has been considered one of the promising technologies in the energy industry and electronic devices. Lithium-ion batteries are fabricated in low-humidity rooms to prevent atmospheric air (moisturizer) from reacting with lithium ions in the electrolyte solution because lithium-ion batteries react easily with air. Single lithium ions react easily with water (H_2O) to produce elemental HF and undesirable products. Therefore, water is an adverse element in the chemical reaction process in lithium batteries. HF can be detrimental to the process because HF degrades the crystal structure of the cathode and anode materials and is parasitic to forming solid electrolyte interphase (SEI) on the surface of the carbon anode. Anodes and cathodes in lithium-ion batteries are made of carbon and lithium oxide. At the same time, the electrolyte is made of lithium salts dissolved in organic solvents [5]. By carefully managing the presence of water

and maintaining appropriate production conditions, the quality and performance of lithium-ion batteries can be ensured, minimizing the adverse effects of HF and maximizing their overall efficiency.

In the last decades, there has been significant interest in non-precious metal-based materials including porous zeolites, metal-organic frameworks, low-energy band gap transitional metal oxides, electroactive carbon-based compounds, and perovskites, have been extensively studied and reported as bi-functional electrocatalysts, photocatalysts, energy storage, and conversion materials [4], [6].

Perovskites, in particular, have gained substantial attention and are considered a leading candidate due to their remarkable properties and potential applications in electrochemical energy devices. Perovskite materials exhibit strong light absorption, high crystalline purity, ease of preparation, and excellent charge transport properties. They also possess increased electrical and ion conductivity, charge storage capacity, and superior catalytic properties [4].

Afterward, Iqbal et al. (2018) was reported one notable application of perovskites is 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 [7].

Perovskites have been extensively studied in various energy systems, including batteries, supercapacitors, photovoltaics, photocatalysis, and electrocatalysis [4], [8]. Their unique properties make them attractive for

improving the performance and efficiency of these devices. The intensive research on perovskites for energy applications reflects the growing interest and potential of these materials in advancing clean and sustainable energy technologies.

PEROVSKITE STRUCTURE

Most of the cathode materials used in rechargeable lithium batteries have a hexagonal layered structure or spinel structure. Cathode materials with high ionic conductivity and high electronics are required for rechargeable batteries with large energy density. One of them uses ABO_3 -type perovskite. Perovskite will be more stable in the pseudo-tetragonal crystal structure, which is between tetragonal and cubic crystal structures as shown in Figure 1 [9].

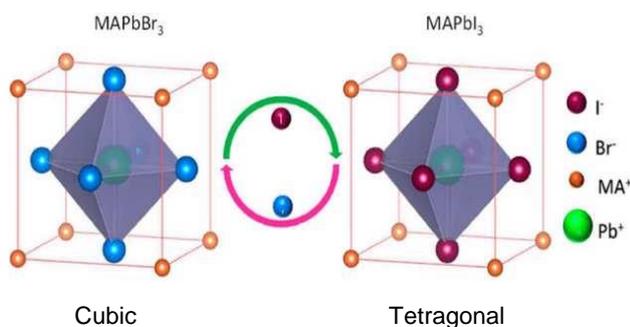


Figure 1. Illustration of the change in crystal structure of cubic perovskite ($MAPbBr_3$) to tetragonal perovskite through the replacement of halide ion Br with I or vice versa ($MAPbI_3$) [9]

Perovskite material is hygroscopic and easily decomposes into its constituents. Perovskite materials have three stable structures at different temperatures, namely orthorhombic, tetragonal, and cubic. The stability of perovskite compounds related to enthalpy of the precursor phase causes differences between halide systems and the condition of each perovskite system. Spin-coating

perovskite materials can show the perovskite crystal structure. Batteries made from mixed halide/inorganic materials with a perovskite structure have attracted the attention of many researchers [10], because it has a relatively high electronic and ionic conductivity [11].

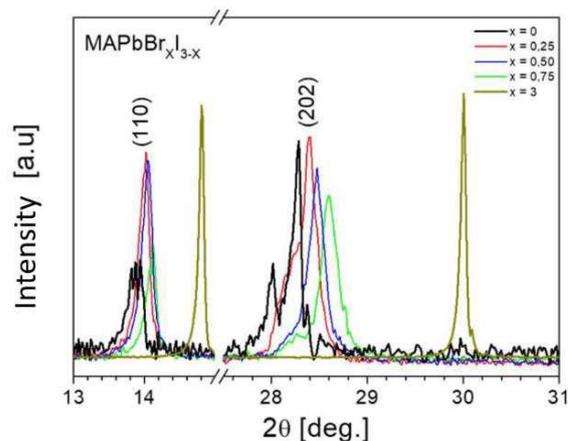


Figure 2. XRD pattern of $MAPbBr_xI_{3-x}$ mixed halide perovskite film [9]

ABO_3 -based perovskite composite oxides with high structural/chemical flexibility are promising multifunctional materials as catalysts [12]. In ABO_3 perovskite-type oxides, the transition metal element (B cation) occupies the center of an octahedron consisting of six oxygen ions. In perovskite type B cations can take different valence states in the range of 3 to 6 [13]. The catalytic properties of perovskite are very useful in developing high-energy storage devices. The surface electronic structure of perovskite is an important factor to promote catalytic activity [14].

In Figure 2 XRD pattern for mixed halide perovskite $MAPbBr_xI_{3-x}$ there is a change in crystal structure from tetragonal $MAPbI_3$ to cubic $MAPbBr_3$. Figure 3 shows the density of the tetragonal state of $MAPbI_3$ and the cubic phase of $MAPbBr_3$, and $MAPbCl_3$ at room temperature. In MA

cations and different crystal structures (tetragonal and cubic) are ascribed to the octahedral tilt of PbI_6 [15]. PbI_2 which is converted into MAPbI_3 has a tetragonal crystal structure, while MAPbBr_3 has a cubic crystal [9].

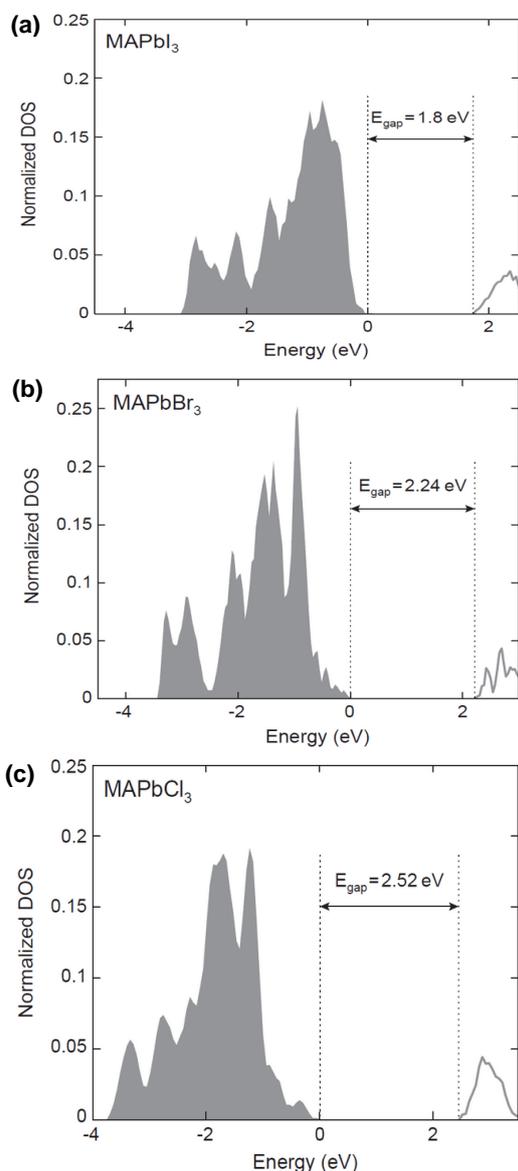


Figure 3. The normalized density of states (DOS) for (a) Tetragonal MAPbI_3 ; (b) Tetragonal MAPbBr_3 ; (c) Cubic MAPbCl_3 [15]

PbTiO_3 crystal structure is an ABO_3 crystal structure, namely cubic perovskite crystals. PbTiO_3 has ferroelectric and

piezoelectric properties (Figure 4) which are needed in microelectronics technology applications due to its high polarization properties. PbTiO_3 is not stable at room temperature so it is necessary to add other elements to improve the desired properties. The addition of elements can cause changes in the crystal structure of PbTiO_3 [16].

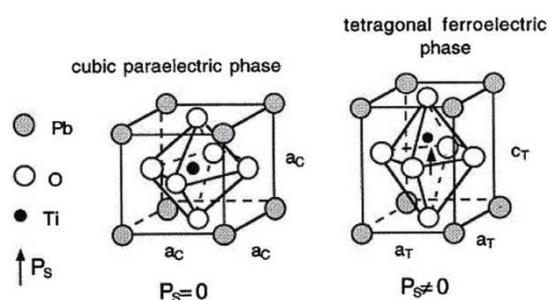


Figure 4. Structure of perovskite PbTiO_3 [16]

Figure 5 shows the XRD patterns on samples with various doping variations of MnO_2 compounds at sintering temperature of 800, 900, and 1100°C. At the addition of MnO_2 0.15 mol, the crystal structure of PbTiO_3 is tetragonal perovskite, at the addition of MnO_2 0.2 mol, PbTiO_3 crystal structure is monoclinic and orthorhombic perovskite [16].

LITHIUM-ION BATTERY (LIB) PEROVSKITE SYNTHESIS

Electrochemical technology has the potential to store energy due to its efficiency. In general, lithium-ion batteries (LIBs) play an important role in large-scale energy storage due to their high specific power ($< 10\text{ kW kg}^{-1}$), energy density ($< 200\text{ Wh kg}^{-1}$), durability (mass life of 3-15 years) and energy efficiency (90-94%) [17]. Some research on the manufacture of anode materials regarding the manufacture of lithium-ion batteries conducted graphite sheets with electrical conductivity ($6.2 \times$

10^{-3} - 43.8×10^{-3} S/cm and conducted research on making $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and soda lime silica anode composites with electrical conductivity of 32.7×10^{-3} S/cm.

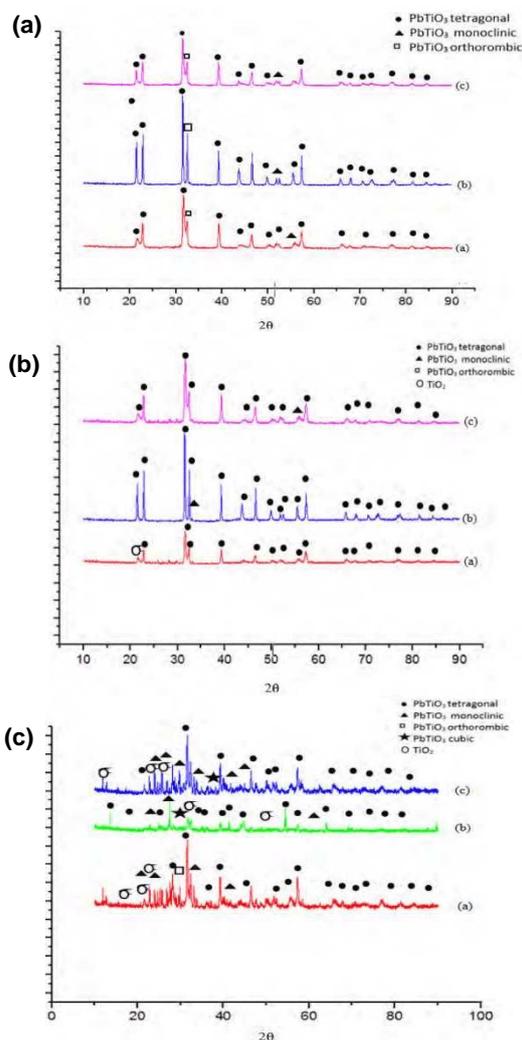


Figure 5. The XRD patterns on samples with various doping variations of MnO_2 compounds at sintering temperature of (a) 800; (b) 900; (c) 1100°C [16]

One of the facile synthesis methods in lithium-ion batteries (LIB) is by using activated carbon raw materials such as rice husk. The rice husk was carbonized at 500°C and then activated used NaOH as activator. After water bath treatment with

HCl, the final rice husk-derived activated carbon (RHAC) was obtained and used as electrode materials in lithium-ion batteries. Schematic illustration of the formation of RHAC shown in Figure 6. The final product exhibits a high reversible capacity around 448 mAh/g after 100 cycles at a rate of 0.2 C, which is a significant improvement of electrochemical performance compared with the non-activated materials [3].



Figure 6. Schematic illustration of the formation of RHAC [3]

Apart from being used as an anode, lithium-ion batteries are also mostly used as cathodes in batteries. Lithium iron phosphate (LiFePO_4) is one of the cathode materials of lithium-ion batteries which has a high theoretical value. Where the synthesis stage is carried out first by synthesizing LiFePO_4/C which is a mixture of 6.495 g LiH_2PO_4 powder, 4.9903 g Fe_2O_3 , and 0.7528 g oil carbon black powder. The powders were combined and calcined at 520°C in a furnace for 6 hours with nitrogen gas. The calcined powder was then heated with temperature variations of 800, 850, 870, and 900°C in a furnace for 16 hours with nitrogen gas flowing. It can be seen that samples at sintering temperatures of 800, 850, 870, and 900°C present diffractogram peaks that resemble commercial LiFePO_4 samples indicating that the samples have formed LiFePO_4 compounds [18]. The

XRD pattern and sintering results shown in Figure 7.

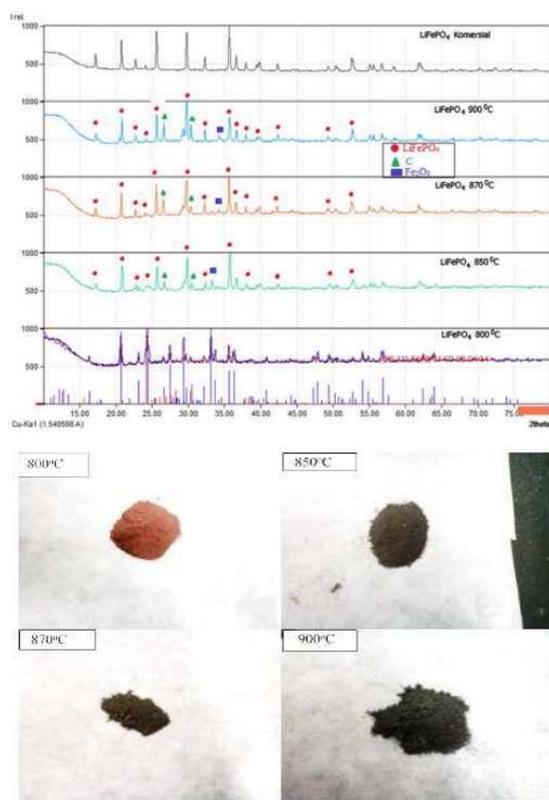


Figure 7. The XRD pattern test results and sintering results of LiFePO_4/C powder [18]

In research conducted by Pratiwi (2018), chitosan, a biopolymer derived from chitin, was used as a base material for the synthesis of solid electrolyte membranes. The study focused on creating a polymer electrolyte solution using a blending method. Chitosan and LiOH were dissolved in 2% CH_3COOH (acetic acid) at different composition ratios, namely 95:5, 90:10, and 85:15. The solution was then stirred using a hot-stirrer device to ensure a homogeneous mixture. Once a homogeneous polymer solution was obtained, it was poured into a plexiglass mold and allowed to dry at room temperature. During the drying process, the solution solidified, resulting in the formation of a membrane. This membrane served as the solid electrolyte in the

system. Chitosan-based solid electrolyte membranes have gained attention due to their potential application in various electrochemical devices, including batteries and fuel cells. The use of chitosan as a base material offers advantages such as its abundant availability, biocompatibility, and good ionic conductivity. By incorporating LiOH, which acts as a source of lithium ions, into the chitosan matrix, the resulting solid electrolyte membrane can facilitate the transport of lithium ions, enabling their efficient use in energy storage and conversion systems. The research conducted by Pratiwi contributes to the development of chitosan-based solid electrolytes and provides insights into the fabrication process of these membranes using a blending method [19].

Figure 8 shows the XRD diffractogram of chitosan before the addition of LiOH, from the diffractogram it can be seen that chitosan has an amorphous phase, while the diffractogram of chitosan after the addition of LiOH shows high conductivity, it can be seen that there is a shift in intensity to be higher which means that the phase shifts slightly to a crystalline phase. This is due to Li^+ ions filling the cavity in the chitosan membrane and causing the conductivity to increase [19].

Several literature studies, that lithium battery anode and cathode materials can be made with activated carbon materials with a sintering process, materials from porous materials (composites), and other materials. Battery performance involves conductive electron transfer, electron transfer occurs from the negative electrode (anode) to the positive electrode (cathode) to produce an electric current and a different potential difference.

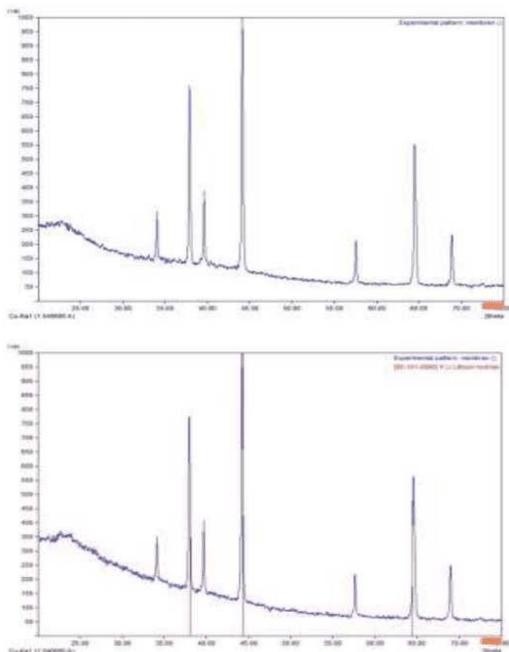


Figure 8. The XRD pattern of chitosan membrane (left); The XRD pattern of chitosan membrane: LiOH (85:15) % w/w [19]

CONCLUSION

Lithium-ion batteries (LIB) are known for their remarkable properties that allowing them as a very promising power source. Most of the electrode materials used in rechargeable lithium batteries have a hexagonal layered structure or spinel structure. Perovskite ABO_3 -type with high structural/chemical flexibility are promising multifunctional materials. Perovskite are highly regarded due to their remarkable properties and their potential applications in electrochemical energy devices, especially as electrode materials for lithium-ion battery.

ACKNOWLEDGEMENT

The authors appreciate and thank to Universitas Palangka Raya for their support.

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