Analysis of the Principle and State-of-art Performances of Perovskite Solar Battery

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Abstract. As a matter of fact, the perovskite has been widely implemented in solar material due to the high convergence efficiency. With this in mind, this paper will analyze the principle as well as the state-of-art performances for the solar battery based on perovskite. To be specific, the brief history of the development of calcite solar cells was given. The basic perovskite crystal structure is shown simultaneously. Two structural types of the Perovskite solar battery: mesoscopic structure and planer heterojunction are introduced. Focus on the performance of the quasi-2D Perovskite Solar Battery. First, this study will show its structure and then show Characterization Methods and Features. The photovoltaic characteristics of Perovskite Solar Cells with various device architectures and various organic amine cations is given. According to the analysis, the applications of Perovskite Solar Battery with Greenhouses Technology as main object is shown. Overall, these results shed light on guiding further exploration of solar material.

Keywords: Perovskite solar battery, quasi-two-dimensional, photovoltaic parameters.

1. Introduction

The issue of energy has always been one of the topics of great importance to people in today's world. Since solar energy is an excellent renewable energy source, people have been trying to utilize to improve the energy problem. Perovskite Solar Batteries are currently among the most promising photovoltaic technologies because of their high-Power Conversion Efficiency and low cost of processing [1]. The perovskite material exhibits good photovoltaic performance because of its excellent semiconductor properties such as high optical absorption coefficient, tunable band gap, low exciton binding energy, excellent carrier mobility and a long carrier lifetime. Perovskite solar batteries' efficiency has dramatically increased over the past few years, going from an initial efficiency of 3.81% to the present certified efficiency of 25.2% [2, 3].

Perovskite was initially found by Russian mineralogist von Perovski in the Ural Mountains' metamorphic rocks in 1839. In 2006 and 2008, perovskite materials CH$_3$NH$_3$PBI$_3$ and CH$_3$NH$_3$PBBr$_3$ were reported and employed as sensitizers in liquid-electrolyte-based DSSC. However, the PCE was only 3.8% [4]. The liquid electrolyte was then replaced with a solid hole-transporting substance known as Spiro-OMeTAD, which resulted in a high-Power Conversion Efficiency of 9.7% and improved the stability of batteries [5]. In 2013, with the research of the material called PTAA which can be acted as Hole transport layer, the PCE could reach 12.3%. In 2016, as the development has been devoted to the study of materials called PSCs, the PCE was boosted to 22.1%.

There are numerous applications for perovskite solar batteries. In the field of industrial production, it can be used as a backup power source and provide clean energy. In the home and commercial fields, it can not only save money but also achieve the purpose of ecological protection. With the continuous progress of perovskite solar battery technology, the scale of perovskite solar batteries used in photovoltaic power stations is getting larger and larger, thus driving the development of the photovoltaic industry. This study will introduce the basic descriptions of perovskite and the principle of Perovskite solar battery. Then, this paper will show the performances of Perovskite solar battery in recent years and discuss about its applications. At last, this research will talk about limitations about Perovskite solar battery.
2. Basic Descriptions of Perovskite

The general structural formula of perovskite materials is $\text{ABX}_3$ (A is organic cation, typically $\text{CH}_3\text{NH}_3^+$, $\text{CH}_2(\text{NH}_2)\text{NH}_3^+$ or their alloys; B is metal cation, typically Pb$^{2+}$, Sn$^{2+}$ or their alloys; X is halogen anion, typically $\text{I}^-$, $\text{Br}^-$, $\text{Cl}^-$ or their alloys) [6]. In $\text{ABX}_3$ crystals, $\text{BX}_6$ forms regular octahedrons, which are connected by a common vertex X to form a three-dimensional skeleton, and A is embedded in the octahedral void to stabilize the crystal structure. Fig. 1 showed the perovskite crystal structure.

![Fig. 1 Perovskite crystal structure.](image)

Metal-organohalide $\text{ABX}_3$ perovskite materials can easily be adjusted by changing $\text{ABX}_3$ component combinations, which is also called bandgap engineering. Firstly, this study will talk about the effect of an ion on the band gap. In cubic perovskite structures, it is generally believed that A does not significantly change the band structure, but changing the size of A ion can regulate the band structure of perovskite in a small range, and larger A ions can cause the expansion of the entire lattice, resulting in a decrease in the band gap. For example, to $\text{APbI}_3$, when A is Cs$^+$, methylammonium (MA$^+$) and formamidinium (FA$^+$), the effective ionic radius is Cs$^+$ < MA$^+$ < FA$^+$, the bandgap is $\text{CSPbI}_3$(1.67eV) > $\text{MAPbI}_3$(1.52eV) > $\text{FAPbI}_3$(1.48eV) [7]. It should be noted that when a smaller metal cation Sn$^+$ than Pb$^+$ is used, the trend of the band gap of $\text{ASnI}_3$ is completely different from that of $\text{APbI}_3$. Then, this study discusses the effect of B metal ion on the band gap. Since Pb is a toxic element and its use is somewhat limited, there is a desire to develop chalcogenide materials that do not contain Pb. B is an excellent option for chalcogenide materials because it belongs to the same group as A in the periodic table. Sn$^{2+}$-based chalcogenides typically have a lower band gap than Pb$^{2+}$-based chalcogenides. In order to ensure that the absorption reaches the near-infrared region, Sn and Pb were combined to create the chalcogenide material. The band gap of the chalcogenide material can be tuned between 1.17eV and 1.55eV by varying the Sn or Pb ratio [8], and the light absorption can be extended to 1060 nm. At last, this study will talk about the effect of halide ion on the band gap. For example, to $\text{CH}_3\text{NH}_3\text{PbX}_3$, as the radius of halogen ions $\text{Cl}^-$, $\text{Br}^-$, and $\text{I}^-$ increases, the bandgap of $\text{CH}_3\text{NH}_3\text{PbX}_3$ decrease gradually ($\text{CH}_3\text{NH}_3\text{PbCl}_3$: 3.11eV [9], $\text{CH}_3\text{NH}_3\text{PbBr}_3$: 2.22eV, $\text{CH}_3\text{NH}_3\text{PbI}_3$: 1.51eV [10, 11]).

3. Principle of Perovskite Solar Battery

The Perovskite solar battery evolved from Dye Sensitized Solar Cells (DSSC), so its device structure is also related to DSSC. There are two structural types of the Perovskite solar battery: mesoscopic structure and planer heterojunction. As for the device structure of perovskite solar battery with mesoscopic structure, if the perovskite material is adsorbed as a dye on the mesoporous TiO$_2$, the device will fail quickly due to the corrosive nature of the liquid electrolyte to the perovskite material. Therefore, park et al. employs Spiro-OMeTAD as a solid hole transport material instead of a liquid electrolyte to solve corrosion-related problems [12]. The mesoporous structure consists of FTO glass, CompactTiO$_2$, TiO$_2$ porous layer, Perovskite absorption layer, Hole transport layer (HTL), and Au electrodes. In order to spin-coat Perovskite nanocrystals into compact TiO$_2$ and create interconnected absorber layers, TiO$_2$ is the most common framework structure.
TiO$_2$ Can not only act as a support, but also act to transport electrons. In addition to the use of TiO$_2$, ZnO nanorods can also be used as framework materials [13], however, the photoelectric conversion efficiency is not as high as that of TiO$_2$.

As for the device structure of perovskite solar battery with planer heterojunction, with the gradual improvement in the quality of perovskite films and the increased awareness of the properties of perovskite materials, perovskite solar battery with planer heterojunction was investigated. The relative simplicity of perovskite solar battery with planer heterojunction compared to perovskite solar battery with mesoscopic structure increases the flexibility of optimization, opens up the possibility of developing stacked structures, and facilitates device research. The most conventional planer heterojunction structure consists of a perovskite absorber layer, an electron transport layer, and a hole transport layer. One of the first attempts to prepare device structures was FTO/ TiO$_2$/CH$_3$NH$_3$PbI$_3$/ Spiro-OMeTAD/Au. The solution method was initially employed for preparation, but due to poor chalcogenide absorber layer quality, the final cell's photoelectric conversion efficiency was low because it could not completely cover the TiO$_2$ substrate and had poor film uniformity (only 1.8%). Subsequently, high quality chalcogenide absorber layers were prepared by evaporation, and the photovoltaic conversion efficiencies were improved to 15.4% [14]. The results show that good photo voltaic conversion efficiencies can be achieved without the use of complex mesoporous structures. If doping TiO$_2$ with yttrium, TiO$_2$ layer will have a higher electron mobility and reduce the work function of ITO, which is beneficial to the injection of electrons from TiO$_2$ layer into ITO. Then through interface modification, planar heterojunction devices short-circuit current and open-circuit voltage are enhanced, and the final photovoltaic conversion efficiency can reach 19.3%. There is also another device structures called PEDOT (PSS/PolyTPD/CH$_3$NH$_3$PbI$_3$/PCBM/Au) [15], which replace TiO$_2$ membranes with PSS. Although the photovoltaic conversion efficiencies of this kind of perovskite solar battery only achieve 12%, it creates a new structure called Inverted plane heterojunction, which provides new ideas for the research of the flexible PCEs.

4. Performance of Perovskite Solar Battery

The stability of perovskite materials has been an issue, although research is helping to increase the photoelectric conversion efficiency of perovskite solar batteries. It is hoped that quasi-two-dimensional perovskite solar batteries would address this issue. Due to their increased thermal stability and hydrophobicity of organic spacer cations, higher crystal formation energies, and more durable structures, quasi-2D chalcogenides will significantly increase the stability of perovskites. In addition, quasi-two-dimensional perovskites also have obvious improvement effects on the morphology of chalcogenide films, which can effectively simplify the process preparation flow.

4.1. Structure of Perovskite Quasi-two-dimensional Solar Battery

The quasi-two-dimensional perovskites were synthesized by replacing or partially replacing the A-site cation in the three-dimensional perovskites with a slightly larger organic amine ion cations in 3D perovskites by replacing or partially replacing them with slightly larger organic amine ions to obtain. Slightly larger organic amine cations slice the chalcogenide crystals along the <100> crystallographic direction and the octahedra $\text{[MX}_6^{4+}$ form inorganic layers. The inorganic and organic amine layers alternating with each other and interconnected by Coulomb forces, forming a quasi-2D dimensional perovskite structure (seen from Fig. 2), including Ruddlesden-Popper and Dion-Jacobson. Currently, the Ruddlesden-Popper perovskite mines exhibit relatively higher stability, whose photovoltaic conversion efficiencies have been more than 18%.

The Ruddlesden-Popper perovskite mines’ chemical composition is $\text{A}_n\text{B}_{n-1}\text{M}_n\text{X}_{3n+1}$ [16]. The value of $n$ is used to tune the performance of the material and the associated photovoltaic cell, and is
called the number of layers of the quasi-two-dimensional perovskite. There are some common Ruddlesden-Popper perovskite mines such as $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ and $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$.

Fig. 2 Structures of two-dimensional, quasi-2D, and 3D perovskites; bandgap arrangement of $\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ and $\text{PEA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ with various $n$ values; common organic amine cations of quasi-2D perovskites;

4.2. Characterization Features of Perovskite quasi-two-dimensional Solar Battery

The hydrophobic organic spacer cations introduced into the quasi-2D perovskites not only prevent water molecules from penetrating into the perovskite lattice and enhance the hydrophobicity of chalcogenides, but also, the quasi-two-dimensional perovskite solar battery exhibits better stability after the addition of the 2D component because the VDW present in the organic amine layer increase the energy needed to remove the Organic ammonium halide for the degradation of perovskites and play a role in impeding perovskite ion movement and migration. The quasi-2D perovskite solar battery shows better stability. After analyzing the semiconductor properties of the prepared$\text{BA}_2\text{MA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$, the results show that the quasi-two-dimensional perovskite structure is flexible and the band gap width and exciton binding energy can be varied with the $n$ value [17]. Therefore, it is possible to change the $n$ value and control the crystal orientation by $n$ value, controlling the crystal orientation, to adjust the behavior of photoelectrons and change the device performance.

However, quasi-2D chalcogenides have exciton binding energies up to hundreds of millielectronvolts and the excitons can be sustained and confined at ambient temperature because of the quantum domain-limiting effect with improved dielectric confinement. The device's optical field is severely constrained by the excitons, which are stable at the room temperature and contained in a built-in electric field made up of a layer that is positively organic and negatively inorganic. It substantially sets a limit to the device's ability to separate photogenerated carriers. A decreased photovoltaic conversion efficiency results from the broad quasi-2D perovskite band gap, narrow spectral absorption range, and reduced carrier mobility brought on by the organic spacer cations that act as insulators. These characteristics all work against the efficient transmission of photogenerated carriers.
After using single-crystal back dissolution technique to film preparation of quasi-2D perovskite, the phase distribution of quasi-2D perovskites can be effectively controlled and realize the thin uniform phase distribution in thin films (as sketch in Fig. 3). The PCE of quasi-two-dimensional Perovskite Solar Batteries has surpassed 18% thanks to improvements in the thin film manufacturing technique, crystal orientation adjustment technology, and device structure optimization. Solar cells made of quasi-two-dimensional perovskite have photovoltaic conversion efficiencies that are already higher than 18% [18, 19]. Some results are listed in Table 1, where PEA means Phenylethylamine iodide; EDBE means 2, 2-(ethylenedioxy) bis(ethylamine); BA means butylammonium; AVA means Aminovaleric acid; 5-AVA means 5-ammoniumvaleric acid; FEA means pentafluorophenylethylammonium; 3BBA means 3-bromobenzylammonium.

![Fig. 3 Pictures of the platy-monocrystal and Bulk single crystal single crystals BA\textsubscript{2}MA\textsubscript{2}Pb\textsubscript{3}I\textsubscript{10} and BA\textsubscript{2}MA\textsubscript{3}Pb\textsubscript{4}I\textsubscript{13}; formation processes of BA\textsubscript{2}MA\textsubscript{n−1}Pb\textsubscript{n}I\textsubscript{3n+1} thin films based on their single-crystalline structures.]

<table>
<thead>
<tr>
<th>2D part</th>
<th>Structure</th>
<th>PCE</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVA</td>
<td>FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/HOOC(CH2)\textsubscript{4}NH\textsubscript{3}PbI\textsubscript{4} − MAPbI\textsubscript{3}/spiro-OMeTAD/Au</td>
<td>14.6%</td>
<td>&gt;200h</td>
</tr>
<tr>
<td>FEA</td>
<td>FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/FEA\textsubscript{2}PbI\textsubscript{4} − FAPbI\textsubscript{3}/spiro-OMeTAD/Au</td>
<td>22.2%</td>
<td>&gt;1000h</td>
</tr>
<tr>
<td>PEA</td>
<td>FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/Cs\textsubscript{0.74}MA\textsubscript{0.13}Pb\textsubscript{1.46}Br\textsubscript{0.39} − PEA\textsubscript{2}PbI\textsubscript{3}/spiro-OMeTAD/Au</td>
<td>20.08%</td>
<td>&gt;800h</td>
</tr>
<tr>
<td>EDBE</td>
<td>FTO/SnO\textsubscript{2}/(EDBE)PbI\textsubscript{4} − (FAPbI\textsubscript{3}+CsI\textsubscript{0.17})Pb(I\textsubscript{0.8}Br\textsubscript{0.2})\textsubscript{2}/spiro-OMeTAD/Au</td>
<td>21.06%</td>
<td>&gt;3000h</td>
</tr>
<tr>
<td>3BBA</td>
<td>ITO/PTTA/3BBAI-MACI-PbI\textsubscript{2}/PCBM/Cr/Au</td>
<td>18.2%</td>
<td>&gt;2400h</td>
</tr>
<tr>
<td>ThMA</td>
<td>ITO/SnO\textsubscript{2}/ThMA-FAPbI\textsubscript{3} − MAPbI\textsubscript{3}/spiro-OMeTAD/MoO\textsubscript{3} − Ag</td>
<td>21.49%</td>
<td>&gt;1800h</td>
</tr>
<tr>
<td>5-AVA</td>
<td>FTO/bl-TiO\textsubscript{2}/mp-TiO\textsubscript{2}/(FAPbI\textsubscript{3})\textsubscript{0.88}(CsPbBr\textsubscript{3})\textsubscript{0.12}/(5 − AVA)\textsubscript{2}PbI\textsubscript{4}/CuSCN/Au</td>
<td>16.75%</td>
<td>&gt;1440h</td>
</tr>
<tr>
<td>PEA</td>
<td>FTO/SnO\textsubscript{2}/FAPbI\textsubscript{3}−PEA\textsubscript{2}PbI\textsubscript{2}/spiro-OMeTAD/Ag or Au</td>
<td>20.64%</td>
<td>1362h</td>
</tr>
<tr>
<td>PDA</td>
<td>ITO/PEDOT:PSS/PDAMA\textsubscript{2}Ma\textsubscript{n−1}Pb\textsubscript{n}I\textsubscript{3n+1}/C\textsubscript{60}/BCP/Ag</td>
<td>13.0%</td>
<td>&gt;1000h</td>
</tr>
<tr>
<td>Ma\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9}</td>
<td>FTO/c-TiO\textsubscript{2}/Ma\textsubscript{3}Bi\textsubscript{2}I\textsubscript{9} − MAPbI\textsubscript{3}/spiro-OMeTAD/Au</td>
<td>18.97%</td>
<td>&gt;800h</td>
</tr>
</tbody>
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5. Applications of Perovskite Solar Battery

Greenhouses are a sophisticated technological tool for modern agricultural production. The regulation of factors like temperature, light intensity, humidity, and CO2 concentration in greenhouses requires energy-intensive means of control, which unquestionably has a significant negative impact on the environment and on economic efficiency. However, greenhouses are also one of the most energy-intensive crop production technologies. Semi-transparent Perovskite Solar Batteries utilize its own energy band gap adjustable, transmittance, high degree of light transmission, flexible and other unique advantages, its development in temperature The development of room agricultural photovoltaic will be very considerable.

Generally, chlorophyll and carotenoids in crop photosynthesis absorb light in the wavelength range of 400nm-550nm and 600nm-1000nm [20], and high-energy photons less than 400nm will have a negative impact on crop growth. For this reason, it would be an ideal greenhouse photovoltaic solution if high-energy photons smaller than 400nm could be filtered out and transmitted through visible light to protect crop growth as much as possible, and the filtered high-energy photons could be utilized to generate electricity. Semi-transparent Perovskite Solar Batteries can precisely meet the above needs, the advantage of its adjustable bandgap can be less than 400 nm light can be fully absorbed, transparent cells will be the crops need to photosynthesis part of the visible light through, and can be prepared on a flexible substrate characteristic, also makes the Semi-transparent Perovskite Solar Batteries can be better to realize the application of the greenhouse.

In 2019, Subhani et al. carried out research for the application of translucent Perovskite Solar Batteries in greenhouse agriculture scenario. Attempts were made to adjust the chemical composition of the perovskite functional layer to prepare ultra-wide bandgap pure bromine component MAPbBr₃ perovskite films [21]. However, such a wide bandgap pure bromine cell has very strict requirements on the film preparation process and quality. Therefore, they compared different anti-solvents in the one-step preparation process, based on the morphology and grain crystallization degree of the chalcogenide films. The final choice of diphenyl tin was based on the morphology and crystallization degree of the grains, the grain growth size, and the difficulty of solvent addition. The final choice of diphenyl ether, which is an effective solvent for the enhancement of the carrier diffusion length of perovskite was improved to further enhance the cell performance. Ultimately, a semi-transparent device with an ultra-wide bandgap of over 2eV, an efficiency of 7.51%, and a transmittance of nearly 40% was realized.

However, if one wants to better apply Semi-transparent Perovskite Solar Batteries to greenhouse agriculture, one needs to prepare Semi-transparent Perovskite Solar Batteries with flexible and bendable characteristics on the basis of meeting the demand of perovskite thin-film components adjusting to the greenhouse light. In 2021, Wang et al. were the first to try to prepare thin metallic transparent electrodes with DMD structure on Semi-transparent Perovskite Solar Batteries and designed application scenarios [22]. By taking advantage of its strong mechanical flexibility and electrical conductivity, a flexible translucent perovskite solar battery, which is different from the traditional steel glass substrate, was realized. The flexible cells achieved a photovoltaic conversion efficiency of 7.67% and a transmittance of more than 60% in the wavelength range of 540~760 nm.

6. Limitations of Perovskite Solar Battery

There are some drawbacks to Perovskite Solar Batteries. First off, the majority of batteries created in laboratories nowadays are very small, measuring only a few millimeters. Crystalline silicon solar batteries, on the other hand, have monolithic sheet diameters of up to 12 cm. Chalcogenide continuous thin film production over bigger surfaces is challenging for laboratories. Second, oxygen has a strong chemical reaction with perovskite solar batteries that damages their crystal structure and releases water vapor that dissolves the salt-like perovskite. The best modern chalcogenides include lead, which could leach out and contaminate the soil and roof to some extent.
7. Conclusion

To sum up, this study introduced the history of the development of the Perovskite Solar Battery and the basic descriptions of perovskite and the principle of Perovskite solar battery. Then, this paper shows the performances of Perovskite solar battery, which focused on quasi-two-dimensional Perovskite Solar Battery. It has good water-oxygen stability and heat stability, and was a new hope for chalcogenide photovoltaic devices to break through current lifetime limitations; this study discusses about its applications, especially on Greenhouses Technology. For the application of greenhouse agricultural scenarios, there is still a lot of room for improvement and research value in terms of device efficiency improvement, flexible preparation, analysis of crop growth and spectral matching, and construction of multi-energy complementary simulation and emulation system under the application of Semi-transparent Perovskite Solar Batteries. At last, this study discusses about limitations about Perovskite solar battery.

References


