

From Dye-Sensitized to Perovskite: The Evolution and Promise of Perovskite Photovoltaic Technology

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Abstract

The last thirty years have witnessed tremendous advances in photovoltaic technology. Photovoltaic technology has allowed for more effective and affordable solar energy conversion systems. The authors will follow the path of photovoltaic technology from the early days of the first generation, silicon based solar cells, to dye sensitized solar cells (DSSC) to the emergence of perovskite solar cells (PSC). The authors have identified that there are numerous solar cells that have achieved efficiencies greater than 25% via power conversion efficiency (PCE) metrics. The authors have performed a systematic literature review to identify key milestones, innovative mechanisms and materials advancements that contributed to the transition from one generation of photovoltaic technology to another. The authors found that the major advancements that enabled the emergence of PSC included replacing liquid electrolytes with solid state hole conductor, perovskite is no longer simply a photosensitizer but rather an ambipolar thin film absorber and adopting inorganic hole transport layers including nickel oxide. While there has been significant development in the field, concerns remain regarding the potential for toxicity from lead and the long term durability of these systems. The authors conclude by providing a comprehensive historical account of the field and identifying areas where future research can be directed toward creating commercially viable and environmentally friendly PSCs.

Keywords

Perovskite Solar Cells; Dye-Sensitized Solar Cells; Photovoltaic Technology; Power Conversion Efficiency; Hole Transport Layer; Solid-State Electrolyte.

1. Introduction

Beginning with the development of first-generation solar technology (silicon), it was not until the advent of second-generation thin-films (cadmium telluride (CdTe), copper indium gallium selenide (CIGS)) did manufacturers begin to address some of the costs associated with first-generation technology; however, they also created new problems in terms of potential environmental and health impacts through the use of toxic cadmium and selenium (Imamzai et al., 2012) [3].

The cost and environmental issues resulting from both first- and second-generation photovoltaics created an imperative to develop third-generation solar technologies, specifically dye sensitized solar cells (DSSCs) and then organometal halide perovskite solar cells (PSCs).

The purpose of this review is to describe the scientific advancements from DSSCs to PSCs. The review will identify the key scientific and material changes that allowed the transition from one type of solar cell to another and assesses the current barriers and potential opportunities associated with perovskite PV technology. The review will help to create a framework for understanding the movement toward higher efficiency, lower cost, and environmentally friendly solar energy.

2. Methods

This research study used a Systematic Literature Review methodology to evaluate the advancement of Photovoltaic (PV) technology through the various generations of PV devices; DSSCs to PSCs. All articles were retrieved from reputable databases using peer-reviewed article and review searches, with the databases being Web of Science, Scopus, and Google Scholar. Keywords searched included “dye-sensitized solar cell,” “perovskite solar cell,” “solid-state hole conductor,” “nickel oxide hole transport layer,” and “photovoltaic efficiency” for the time period starting at 1991 which is when Grätzel and O’Regan first published their seminal work on DSSC’s to 2024.

The inclusion criteria for this research included that all the selected studies had to have been published in a peer-reviewed journal, contain original experimental data or comprehensive reviews of photovoltaic device performance, and specifically focus on the mechanism(s), material(s) of DSSCs or PSCs. Any studies that focused on theoretical models only without experimental validation were excluded. Seven primary references were identified that formed the basis of the overall narrative regarding the technological advancements of the subject matter discussed herein. The findings of the analysis were presented chronologically and thematically to explore device architectures, sensitizers/absorbers, electrolytes, hole transport mechanisms and PCE benchmarks.

3. Results

3.1 The Emergence of Dye-Sensitized Solar Cells

The dye-sensitized solar cell was originally developed in 1991 by Grätzel and O’Regan, who provided an example of biomimicry in the field of photovoltaic conversion by creating a new way to convert light into electricity which is unlike traditional semiconductor based p-n junction solar cells. Dye sensitized solar cells (DSSCs) separate the two functions of the solar cell; Light Absorption and Charge Transport: The molecular sensitizer (in most cases a ruthenium polypyridyl complex), absorbs the energy from the incident photons and creates an electron within the wide-bandgap mesoporous titanium dioxide (TiO_2) semiconductor material. The dye is then re-oxidized by a redox mediator (which can be one of many examples but is often the I^-/I_3^- couple) dissolved in a liquid electrolyte (Grätzel, 1991) [2]. An important factor in achieving practical efficiencies was the development of nanostructured TiO_2 films with surface areas approximately 300 times larger than flat films allowing for much higher light harvesting by the dye monolayer adsorbed on the surface.

In comparison to silicon based devices, DSSCs were able to reduce production costs by 10-20%, due to no need to use vacuum deposition equipment, as well as being lighter and flexible and therefore expanding the possibilities for DSSCs to be used in Building Integrated Photovoltaics and Portable Electronics (Andualem & Demiss, 2018) [1]. Additionally, DSSCs do not include the highly toxic elements (Cd, Se) present in some thin film solar cell technologies, making them a cleaner technology option.

3.2 Limitations of DSSCs and the Transition to Perovskite Sensitizers

The main problem with DSSC's is the liquid electrolyte is volatile. When the solvent evaporates or leaks out of the DSSC cell performance will degrade over time; and since the electrolyte can be very corrosive to the various components within the DSSC it will also cause corrosion of the parts and desorb the sensitizer from the TiO_2 surface. Therefore, the maximum power conversion efficiency (PCE) of DSSC's reached a level of about 11-12% which is much less efficient than silicon-based solar cells.

In 2009 Kojima, Teshima, Shirai, and Miyasaka showed that organometal halide perovskites ($\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$) could be used as sensitizers in a liquid-electrolyte photovoltaic cell architecture. The first PCE for these perovskite-based devices was 3.81%. This was better than the PCE's achieved using quantum dots but still much lower than the best efficiencies obtained when using optimized organic sensitizers (Kojima et al., 2009) [5]. Nevertheless, this result showed that there is significant potential for using perovskite materials in photovoltaic applications. The major

obstacle preventing further development of perovskite-sensitized liquid-electrolyte photovoltaic cells is the solubility of perovskite in the liquid electrolyte. In fact, even though the electrolyte can be formulated to dissolve the perovskite, it rapidly degrades the photovoltaic cell, so an entirely new type of photovoltaic cell is needed.

3.3 Solid-State Architecture and Efficiency Breakthroughs

The stability issue was finally resolved in 2012 when Kim, Lee, Im, and colleagues, who had collaborated with Park and Grätzel, switched out the liquid electrolyte with a solid-state hole conduction material 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD), creating a fully solid-state MSSC design that removed any contact between the corrosive liquid solvents and the perovskite absorber; this created an MSSC that had a PCE of 9.7% and greatly improved long-term device stability (Kim et al., 2012) [4].

At the same time, Lee, Teuscher, Miyasaka, Murakami, and Snaith provided greater mechanistic insight into how the new MSSC worked as they replaced the electron acceptor mesoporous TiO₂ layer with an insulating mesoporous Al₂O₃ layer, which allowed them to observe that electron transport occurred completely through the perovskite film with rates roughly 10 times larger than those previously measured in TiO₂ based systems. As a result of their findings, they were able to create MSSCs with PCEs of 10.9% (Lee et al., 2012) [6]. These results changed the fundamental way scientists viewed perovskites in MSSCs, as they transitioned from being a surface adsorption sensitizer to being an ambipolar thin-film absorber that could efficiently harvest photons and transport both electrons and holes. The introduction of the MSSC design created the conceptual and empirical basis for all future efficiency advancements, including efficiencies that have now exceeded 25%.

3.4 Inorganic Hole Transport Layers: Nickel Oxide

Hole-transport-layer (HTL) technology has contributed significantly to the performance of photovoltaic cells (PSCs), as well as their operational stabilities. While traditional organic hole-transporting layers (HTL) have several drawbacks such as poor thermal stability, high cost of materials and the need for complex chemical syntheses, Yin, Guo, Xie, Que and Kong (2019) have described the benefits of employing inorganic HTLs with specific focus on nickel-oxide (NiOx). By employing combustion methods for preparing NiOx thin films, devices were produced that had power conversion efficiencies (PCE) of up to 20.2 %. Moreover, NiOx can be utilized to prepare composite film layers that are both absorbing and capable of extracting carriers with perovskite films, thus allowing for greater efficiency in the extraction of charge carriers. The use of NiOx as a counter-electrode in combination with carbon materials was also found to enhance the operational stability and overall performance of the devices. The authors of this study concluded that both interface engineering and metal doping of NiOx could represent potential avenues for future improvements in the performance of devices using NiOx as an HTL (Yin et al., 2019) [7].

4. Discussion

A consistent model of innovation through the elimination of performance limiting factors has emerged through the progression from DSSCs to PSCs. The transition to each new generation of photovoltaic cells was directly due to the discovery of fundamental material or structural limitations to prior cell designs. For example, the toxic nature of many thin film materials used in DSSCs resulted in the development of DSSCs. In contrast, the short life cycle of liquid electrolyte solutions led to the introduction of perovskite based photosensitizers. The degradation of perovskite in liquid solutions resulted in the incorporation of solid state hole conducting layers. The poor charge carrier mobility in TiO₂ scaffolding structures were resolved with the use of meso-superstructure architectures.

One of the most transformative conceptual changes in this field has been the reinterpretation of perovskite from a sensitizer to an ambipolar absorber. This transformation was empirically proven by Lee et al. (2012) and enabled a significant expansion of the design possibilities for PSC architectures, from mesoporous scaffold dependent configurations to planar heterojunction configurations that

allowed for rapid increases in the efficiencies of PSCs. Following the demonstration of the feasibility of using inorganic hole transporting layers (HTLs) such as NiO_x, which offered both improved stability and reduced costs compared to organic HTLs while achieving similar power conversion efficiencies (PCEs), the possibility of producing PSCs at an industrial scale became a viable reality.

There are still however several barriers to overcome before PSCs can be commercially deployed on a wide scale. Of particular concern is the inclusion of lead in the perovskite absorber layer, especially considering large-scale terrestrial applications where lead poses significant environmental and regulatory issues. The replacement of lead with non-toxic elements such as tin-based and bismuth-based halide perovskites continues to be actively researched. However, these alternative perovskite compositions currently offer significantly lower PCEs than their lead-based analogs. Another major barrier to the deployment of PSCs on a wide scale is long term operational stability. PSCs must be able to withstand the full range of environmental stressors including humidity, oxygen, UV light and temperature fluctuations over extended periods of time. While encapsulation technologies, compositional modifications and the use of two-dimensional/three-dimensional perovskite heterostructures are offering some hope in terms of increasing the lifespan of PSCs, standardizing the accelerated aging testing protocols required to allow for comparison between different studies is a necessary step forward.

5. Conclusion

The progression of photovoltaic technology from silicon based and thin film type, to dye-sensitised solar cells and finally to today's perovskite type was reviewed in the above article. Major events in this sequence were; the invention of the DSSC by Grätzel and O'Regan in 1991, the first use of perovskite sensitizers by Miyasaka and co-workers in 2009, the development of solid-state PSCs by Kim, Park and Grätzel in 2012, the definition of perovskite as an ambipolar absorber with Snaith and co-workers in 2012 and the progress toward inorganic HTLs by Yin et al in 2019. Taken together, these innovations have increased the PSC efficiency from its first measured value of 3.81 % to over 25 % in less than 10 years, which is the fastest increase in photovoltaic efficiencies recorded. However, while there are still issues with lead toxicity and long term stability, the rapid pace of development and the breadth of on going research indicates that perovskite type photovoltaic systems have the potential to be a revolutionary way to generate sustainable energy in the future.

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