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State of the art and future outlook on solid state electrolytes for dye sensitized solar cells

Explain various energy sources and their
conversion from a chemical perspective

Bachelor's thesis in MLREAL
Supervisor: Solon Oikonomopoulos
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Abstract

Solar cells are used to harvest one of the most abundant clean and renewable energy source, solar power. After decades of research, silicon based solar cells remains as one of the most popular solar cells, boasting high performance and a continuous decline in production cost. A low cost alternative, using environmentally friendly, non-toxic, lead-free, and cheap materials is dye sensitized solar cells (DSSC). The DSSCs with the highest performance uses a liquid electrolyte, but has issues with the long term stability due to leakage of the electrolyte. To address these issues and improve the stability of the DSSCs, the electrolyte was replaced with a solid state conductor called a hole transporting material (HTM). The efficiencies of these cells however, remained low for a long period of time hindering their commercialization. In recent years, all solid-state DSSCs (ssDSSC) have improved, and their efficiency is now almost equal to their liquid counterparts. Despite the improved stability, their long-term stability is still not adequate which remains as one of the big barriers for commercialization. Here ssDSSCs with high efficiency using different state of the art HTMs are highlighted, and the long-term stability of these cells discussed and how the future of this technology looks in terms of commercialization and stability.

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1. Introduction

To combat climate change, the significance of renewable energy and energy efficiency has been emphasized in the United Nations Climate Change Conference (25). Harnessing the power from the sun using photovoltaic devices has therefore become a major focus point in politics and research recently as it is the most abundant clean and renewable energy source available (14, 20). Solar cells using silicon has become one of the most known solar cells showing efficiencies up to 20-30% along with other thin-film solar cells (14, 15, 18). To overcome one of the most significant obstacles to expedite the growth of renewables, cheaper solar cells using cost efficient materials called dye sensitized solar cells (DSSC) is an alternative (14, 25). State of the art DSSCs have shown efficiencies reaching up to 14.2% using a liquid electrolyte under one sun illumination (26). The usage of liquid electrolyte has however been its limiting factor for large scale production of these highly efficient DSSCs due to their upscaling and long-term stability issues (6). The source of the long-term stability issues comes from difficulties of sealing the liquid junctions between the working electrode (WE) and the counter electrode (CE), evaporation of electrolyte, and corrosion of the electrode materials (14). A solution to this problem is to replace the liquid electrolyte with a hole transporting material (HTM) to create solid-state dye sensitized solar cells (ssDSSC) which has been under extensive research for multiple decades (14, 15). The efficiency of these cells is however lagging slightly behind its liquid counterpart, with the highest efficiency recorded being around 12% with a theoretical value predicted to be approximately 20% (4, 15). The long term stability of different HTM used in ssDSSCs has rarely been reported, with some showing very poor stability (6, 20, 22, 24). This could be due to there not being a standardized testing protocol for ssDSSCs in contrast to silicon solar cells which limits the comparison between the stability of HTMs in different reports as they usually use a wide range of testing methods (3, 4, 14, 20, 22, 24). The length of the different stability tests varies from 200-1500 hours, some reports test their solar cells at elevated temperatures while soaking sunlight, while others store their cells for long periods of time in darkness. This review highlights different solid state electrolytes, both inorganic and organic with high efficiency and discusses the long-term stability of ssDSSCs using these electrolytes. The importance of the long-term stability in future research for commercialization of ssDSSCs is also highlighted.

2. Theory

2.1 Device construction and working principles

Solid-state dye sensitized solar cells (ssDSSC) normally consists of a photoanode or working electrode (WE), a counter electrode (CE), dye sensitizer and a hole transporting material (HTM) (14, 15). These components are stacked in layers as shown in Fig. 1 and differs slightly from a DSSC using a liquid electrolyte as a charge transport because spacers and further sealing between the electrodes is not needed (14). The outermost layer in a ssDSSCs consists of a glass substrate coated with a fluorine doped tin oxide (FTO) (14). This substrate should have a transmittance above 80% to allow the effective area of the cell to receive optimal amount of sunlight (15). It also needs to have high electrical conductivity for efficient charge transfer and reduced energy loss. Nanoporous metal oxides is then deposited onto the glass substrate to finish the WE (14). Examples of some metal oxides used as a semiconductor is TiO_2 , Nb_2O_5 , ZnO , SnO_2 (n-type), and NiO (p-type) with a mesoporous anatase allotropic form of TiO_2 being most commonly used as a semiconductor (14, 15). This is because TiO_2 is non-toxic, less expensive, and easily available (15). In addition, the high surface area from the 20-30 nm particles allows for a large interface between the dye and the nanostructured TiO_2 (14).

The dye sensitizer which plays a crucial role by absorbing the incoming light in the ssDSSC requires some photophysical and electrochemical properties (15). These dyes can be categorized into organic dyes and metalorganic complexes (14). The dye should absorb the region between ultraviolet and near-infrared light and be luminescent (15). The highest occupied molecular orbital (HOMO) should lie lower than the HOMO of the electrolyte to ensure efficient electron transfer, but far from the surface of the conduction band of the semiconductor to prevent charge recombination (15). In contrast, the lowest unoccupied molecular orbital should lie as close to the conduction band, but higher to allow for electron injection into the semiconductor (15). The HTM infiltrates the porous metal oxide and is responsible for the

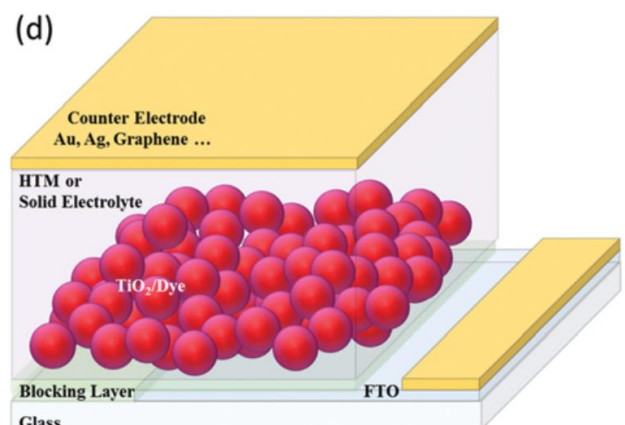


Fig. 1: Schematic sketch of solar cell architecture for the assembly of ssDSSCs (14).

regeneration of the dye by transporting the holes to the CE (14). Ensuring adequate amounts of HTM as a layer on top of the TiO_2 is important as a thin layer can create pinholes resulting in the CE contacting the mesoporous TiO_2 film (14). However, a thicker layer will in turn cause an increased series resistances occurring in the solar cell (14, 15). The structure of different HTM is shown in Fig. 2. To avoid direct contact between the FTO and HTM a blocking layer is deposited on top of the FTO where a compact layer of sintered TiO_2 is mostly used (14).

For the solar cell to convert sunlight into useable energy, the different components in the cell need to work together. The dye, which is bound to the semiconductor, mostly TiO_2 or ZnO , absorbs photons from light (14). The energy the dye receives from absorption is enough to excite electrons from the HOMO, to the LUMO which can be used to inject the electron to the conduction band of the semiconductor (14). After injection, the semiconductor moves the electrons to the FTO electrode by diffusion (14). Since the electrons the semiconductor receives are injected from the dye, it becomes oxidized and needs to be regenerated to inject a new electron (14, 15). In a ssDSSC the HTM is responsible for regenerating the oxidized dye, and since the HOMO of the HTM is higher than the HOMO of the dye, the holes will be positioned in the HTM after injection. The holes are then transported to the CE (14). The process can be summarized in 5 different steps as illustrated in Fig. 3, each process occurring in different timescales (14). The initial first step is the excitation of the dye from absorbing light (14). The excited dye then injects an electron (step 2) into the conduction band (step 3) of the semiconductor. The dye is then regenerated (step 4) and the hole is transported to the CE via the HTM where the HTM is regenerated (step 5) (14). The fastest process in the cell, is the

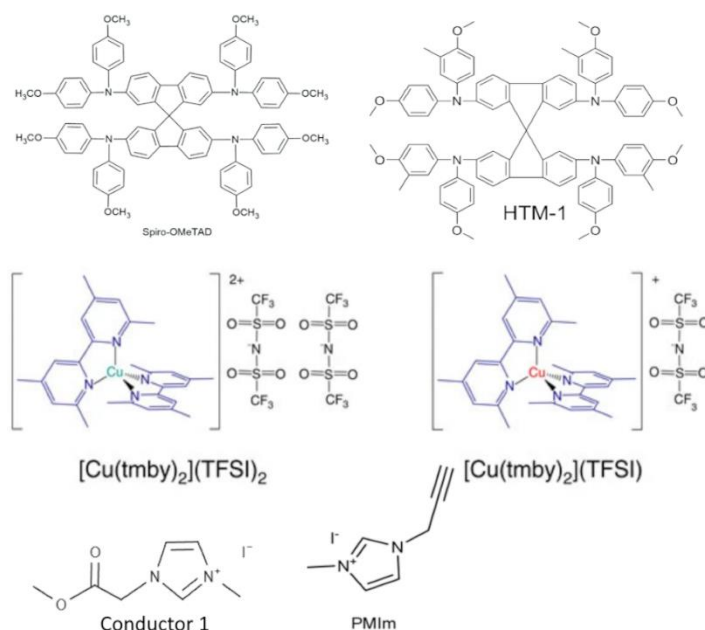


Fig. 2: Chemical structures of organic hole transport materials mentioned in this review (3, 14). Reprinted (adapted) with permission from (20, 22). Copyright 2015, 2013 American Chemical Society.

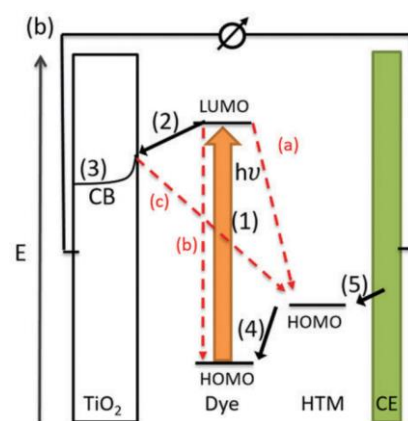


Fig. 3: Schematic drawing of charge transport mechanisms in a ssDSSC (14).

electron injection and hole injection which occurs in around femto- to picoseconds with dye regeneration being the slowest, taking a few hundred picoseconds (14). The dye regenerates orders of magnitude faster than in a liquid junction solar cell occurring on the microsecond scale, due to the rapid hole injection into the HTM. Fig. 3 also illustrates the charge recombination processes which reduce the efficiency of the cell, from the dye (a) to the HTM, semiconductor (b) to the HTM and from the dye (c) back to the dye (14).

2.2 Photovoltaic parameters

The power from the cell generated can be used to measure and calculate the efficiency and performance of the cell, these parameters are called: open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), power conversion efficiency (PCE or η) and incident-photon-to-current conversion efficiency (IPCE) (14,15). The V_{OC} is measured across the electrodes at zero milliampere current in an open circuit or the potential difference in fermi levels between the semiconductor and HTM (14, 15). The current generated from the cell when the electrodes are short circuited at zero volts is the short circuit current and is usually normalized by the area of the solar cell to give the short-circuit current density J_{SC} (14, 15). The ratio between the maximum power output of the cell (P_{max}) and the product of the J_{SC} and V_{OC}

$$FF = \frac{P_{max}}{J_{SC} \times V_{OC}} \quad (1.1)$$

is called the fill factor (15). Formula 1.1 can be rearranged and used to describe the efficiency of the cell

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \quad (1.2)$$

as the ratio between P_{max} and the incoming light power P_{in} (14, 15). Lastly, the incident-photon-to-current conversion efficiency is determined by the ratio of electrons flowing through the circuit to the number of photons incident on the surface at any wavelength but can also be defined as the product of the efficiencies of the required process (14, 15).

$$IPCE(\lambda) = LHE(\lambda) \varphi_{inj}(\lambda) \varphi_{reg}(\lambda) \varphi_{cc}(\lambda)$$

The efficiencies include light harvesting efficiency (LHE) dye regeneration (φ_{reg}), electron injection (φ_{inj}) and charge collection at the electrode (φ_{cc}) (14). Since the efficiencies are recorded at a specific wavelength the IPCE is usually represented in a wavelength spectrum (14).

3. Discussion

Table 1: Photovoltaic parameters of different ssDSSCs under standard one sun AM 1.5G illumination, the chemical structures of the different dyes are shown in Fig. 4.

CE ^a	Sensitizer	HTM ^b	Additives ^c	V _{OC} ^d [mV]	J _{SC} ^e [mA cm ⁻²]	FF ^f	PCE ^g [%]
Ag	Y123	Spiro-OMeTAD	Li, <i>t</i> BP, Co	986	9.5	0.76	7.2 (16)
Au	N719	Spiro-OMeTAD	Li, <i>t</i> BP, Sb	931	4.6	0.71	3.2 (17)
Ag	AQ310	Spiro-OMeTAD	Li, <i>t</i> BP, TeCA	870	12.3	0.75	8.0 (9)
Ag	AQ309	Spiro-OMeTAD	Li, <i>t</i> BP, TeCA	820	11.5	0.72	6.8 (9)
Ag	LEG4	Spiro-OMeTAD	Li, <i>t</i> BP, TeCA	880	11.4	0.73	7.3 (9)
Ag	ID504	Spiro-OMeTAD	Li, <i>t</i> BP	760	9.76	0.64	4.8 (20)
Ag	ID504	HTM1*	Li, <i>t</i> BP	820	9.34	0.63	4.8 (20)
Pt	N719	CsSnI ₃	SnF ₂	732	19.2	0.73	8.5 (1)
Pt	N719	CsSnI ₆	Li, <i>t</i> BP	631	14.7	0.68	6.3 (23)
PEDOT	Y123	Cu(tmby) ₂	Li, <i>t</i> BP	1080	13.87	0.73	11.0 (3)
PEDOT	WS-72	Cu(tmby) ₂	Li, <i>t</i> BP	1070	13.8	0.79	11.7 (4)
Pt	MK2	PMIm	None	710	12.65	0.70	6.3 (22)
Pt	-	Conductor 1	I ₂ , LiI, EMIm ⁺ BF ₄ ⁻	660	13.77	0.73	6.6 (7)

* Asymmetrical spiro-OMeTAD. ^a Counter electrode. ^b Hole transporting material. ^c List of additives: Li = LiTFSI, *t*BP = 4-*tert*-butylpyridine, Co = FK102, Sb = N(PhBr)₃SbCl₆, TeCA = 1,1,2,2-tetrachloroethane, EMIm⁺BF₄⁻ = 1-methyl-3-ethyl-imidazolium tetrafluoroborate. ^d Voltage of open circuit. ^e Current of shorted circuit. ^f Fill factor. ^g Power conversion efficiency.

The most common redox couple in a liquid electrolyte is I⁻ and I³⁻, however its long term durability and performance is affected because it is corrosive, volatile and photoreactive (1, 5, 6). This causes the liquid electrolyte to react with different metallic compounds and sealing materials which in turn will lead to electrode corrosion and electrolyte leakage. Using a solid state electrolyte will however not have these types of problems. Because the use of a solid state electrolyte in a DSSC is more stable than a liquid electrolyte using I⁻/I³⁻ as a redox pair, it could be cheaper to use the former to prevent replacement or repair costs of the solar cells.

A solar cell using CsSnI₃ doped with SnF₂ shows similar efficiency as the highest performing N719-dye-containing Grätzel cell (PCE ≈ 11%) without the use of liquid electrolyte and the consequences of such an electrolyte. It has been shown that CsSnI₃ is well fitted for a p-type direct bandgap semiconductor in an all-solid state inorganic solar cell because of its energy gap of 1.3 eV and high hole mobility of $\mu_h = 585 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature (1). Other components in the solar cell system included a n-type nanoporous TiO₂ with the dye N719 (*cis*-diisothiocyanato-bis(2-2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis-(tetrabutylammonium)) (1). When the solar cell including CsSnI_{2.95}F_{0.05} was further doped with 5% SnF₂, the TiO₂ nanoporous film pre-treated by a fluorine plasma and two layers of the three dimensional inverse photonic crystal ZnO applied over the CE, the solar cell showed a power conversion efficiency (PCE) of 10.2% (8.5% with mask) compared to the

Grätzel cell with around 11% efficiency (1). This relatively high efficiency proves that solid state DSCs can perform just as good, if not better than DSCs using a liquid electrolyte, and its efficiency can be explained and understood from the process used to fabricate the cell.

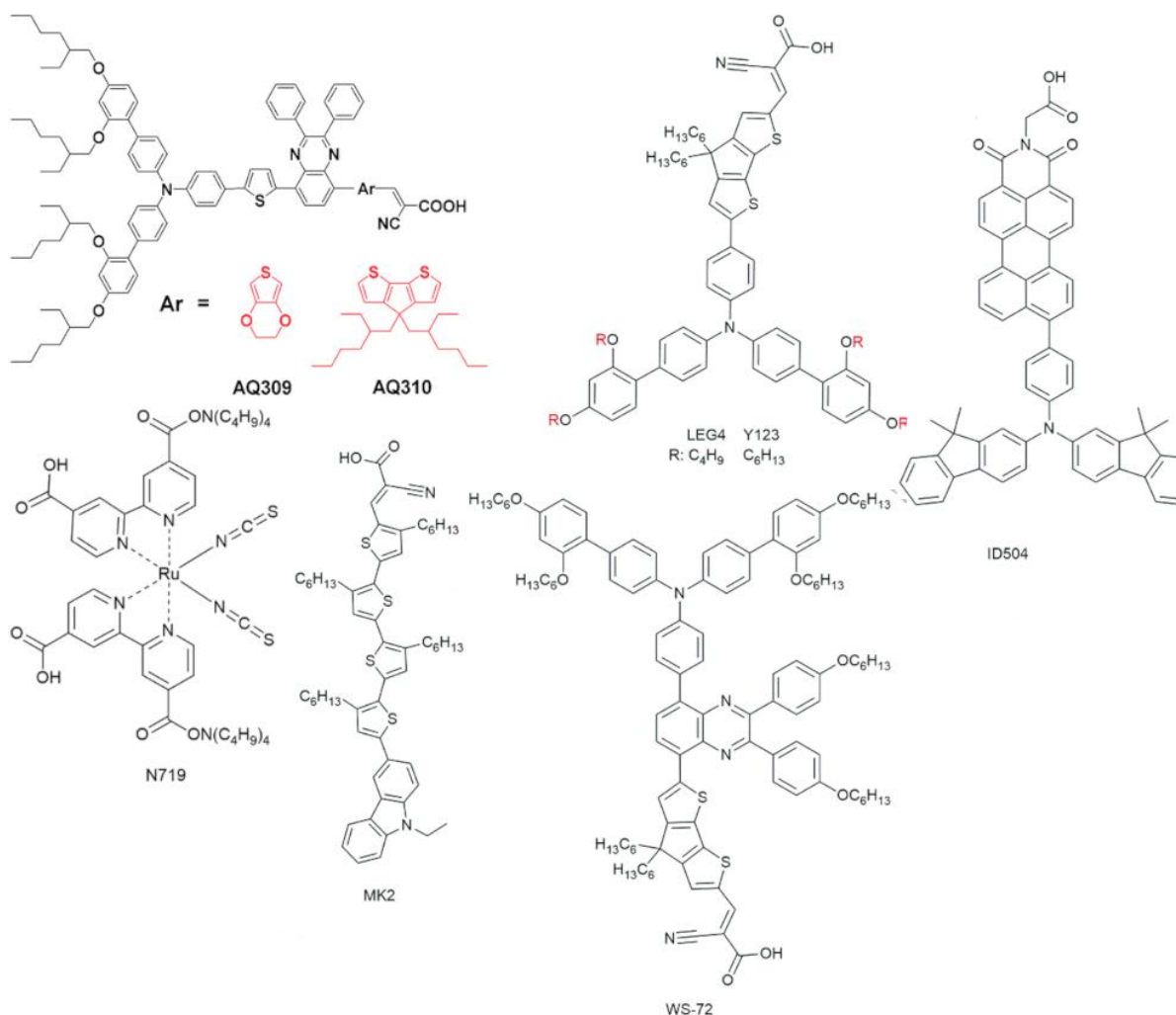


Fig. 4: Chemical structures of different sensitizers used in ssDSSCs (9, 14).

The fabrication procedure for the inorganic hole transfer material (HTM) is simple, facile, inexpensive and does not require high-vacuum deposition processes, complex chemical reactions, or high-temperatures (1). The first step is to synthesize $\text{CsSnI}_{3-x}\text{F}_x$ ($0 \leq x \leq 1$) by heating the correct stoichiometry of Cs, SnI_2 and SnF_2 to 450 °C for 30 minutes in an evacuated Pyrex or fused silica tube before its quenched to room temperature (1). The powder can then be dissolved in anhydrous polar organic solvents and appropriate ratios of $\text{CsSnI}_{2.95}\text{F}_{0.05}$ and SnF_2 can be mixed for doping (1). To finish the preparation of the hole conductor, the solution was added into the cell with a micropipette and dried (1). Since the last step of the process involves using a liquid, the hole conductor is more likely to get

adsorbed in the nanopores of the TiO₂ electrodes. This can allow the HTM to homogeneously infiltrate the TiO₂ scaffolding which is one of the main problems for solid-state DSSCs (1).

Another inorganic hole conductor with a similar fabrication process is a blend of [Cu(4,4',6,6'-tetramethyl-2,2'-bipyridine)₂](bis(trifluoromethylsulfonyl)imide)₂ (Cu(tmby)₂TFSI₂) and [Cu(4,4',6,6'-tetramethyl-2,2'-bipyridine)₂](bis(trifluoromethylsulfonyl)imide) (Cu(tmby)₂TFSI) (2). To synthesize the Cu(tmby)₂TFSI₂ complex, 1 part of CuCl₂ can be mixed with 3 parts tmby in ethanol at room temperature under nitrogen atmosphere for 2 hours (2). The green powders can then be filtered and redissolved in deionized water before an addition of 5 parts LiTFSI (2). After 2 hours of stirring under nitrogen atmosphere at room temperature the green complex can be collected by filtration and washing with water (2). The synthesis of Cu(tmby)₂TFSI is identical to the synthesis of Cu(tmby)₂TFSI₂, other than the usage of CuI instead of CuCl₂ (2). The last step involves dissolving the complexes with a concentration of 0.06M and 0.2M of [Cu(tmby)₂](TFSI)₂ and [Cu(tmby)₂](TFSI), respectively, along with 0.6M 4-*tert*-butylpyridine in acetonitrile (3). After injecting the electrolyte, the solvents can slowly be evaporated (3). The main difference between the preparation of this HTM and the HTM containing CsSnI_{2.95}F_{0.05} is the preparation of the pure complexes, and that the HTM based on copper contains two different complexes. The difference in preparation causes the preparation time of [Cu(tmby)₂](TFSI)_{1 or 2} to be around 2 hours, while the CsSnI_{2.95}F_{0.05} can be prepared in around 30 minutes (1, 2, 3).

Despite the longer preparation time, using a blend of [Cu(tmby)₂](TFSI)₂ and [Cu(tmby)₂](TFSI) as a HTM, Y123 as a sensitizer and electrodeposited PEDOT (poly(3,4-ethylenedioxythiophene)) as a CE has shown a PCE of 11.0% (3). A surprising result is that the DSSC using a liquid electrolyte containing the two copper complexes showed a lower average J_{SC} (13.17 mA cm⁻²), PCE (9.3%) and FF (0.66) than the corresponding ssDSSC using the complexes as a HTM with an identical V_{OC} of 1.07 V (3). The ssDSSC showed an average J_{SC}, PCE and FF of 13.70 mA cm⁻², 10.2% and 0.696, respectively, however the standard deviation of the J_{SC} had a larger variance (3). The reason for the increase in variance is due to the crystallinity of the copper complexes, where an amorphous HTM showed a larger J_{SC} than the crystalline due to the likelihood of holes in the crystalline HTM to get trapped at the crystal grain boundaries, resulting in reduced hole mobility (3). The PCE of a ssDSSC using copper complexes has shown a small increase with the usage of a different dye called WS-72 (4). For liquid electrolytes, this dye limits the voltage lost due to an over

potential of the electron transfer from the photoexcited dye to titanium dioxide with better alignment between the LUMO of the dye and the conduction band (4). However, for the ssDSSC the V_{OC} was slightly lower despite the improvements to the dye and the increased FF led to the significant increase in the PCE (4).

An interesting result from a solid state ionic conductor used as a HTM is the long term stability of the PCE, remaining at 100% of its value after 1000 h of one sun soaking (7). The ionic conductor consists of 1-(2-methoxy-2-oxylethyl)-3-methyl imidazolium iodide, I_2 , LiI and 1-methyl-3-ethyl-imidazolium tetrafluoroborate ($EMIm^+BF_4^-$) as a crystal growth inhibitor with a metal free organic dye (7). The ssDSSC also showed a good PCE of 6.63% with a FF of 0.73, the high FF is believed to be caused by the 3D ionic channel however it is not clear yet (7). The ionic conductor without the addition of $EMIm^+BF_4^-$ showed crystal formations on the solid electrolyte inhibiting the filling of the pores in the TiO_2 layer, causing a PCE of 2.29% (7). The wide gap between the PCE of a ssDSSC which contains crystals in the electrolyte and one which does not, shows the importance of scanning the solid electrolyte for crystal growth and preventing it by either adding an inhibitor or using different ions or HTMs which does not crystallize as easily.

To synthesize 1-(2-methoxy-2-oxylethyl) imidazolium, sodium can be added to a flask containing absolute dry methanol equipped with a condenser tube and stirred for 2 hours (7). Then equal amounts of imidazole can be added to the mixture under nitrogen, heated to 50 °C and stirred for another hour (7). Equal parts methyl chloroacetate can then be added dropwise to the solution and the system can be kept at 50 °C for 16 hours before it is cooled to room temperature (7). When the reaction is finished and filtered, the solvent can be evaporated until viscous oil remains (7). 2 parts of crude product can then be dissolved in methanol along with 1 part alkyl iodide and stirred at room temperature for 48 hours before reprecipitating it in diethyl ether twice to finish the synthesis (7). To apply the solid electrolyte in the solar cell, it can be repeatedly injected into the interspace between the working and the counter electrode and dried on a hot plate at 50 °C until the TiO_2 is filled with solid-state electrolyte before drying for another hour on the hot plate (7).

An organic HTM which does not have a simple synthesis, is 2,2',7,7'-tetrakis(N,N-di(4-methoxyphenyl)amino)-9,9'-spirobifluorene (Spiro-OMeTAD) which includes 5 different steps resulting in an overall yield of around 50% after an improved synthesis route (8). Different dye sensitizers have been used to create solar cells with this HTM, with the highest

resulting in a PCE of 8.0% (9-11, 16, 17, 20). The solar cell achieving a this PCE used AQ310 as a dye, which has a broader light-absorption spectrum and better at retarding charge-recombination losses compared to the LEG4 dye (9). Spiro-OMeTAD is still limiting the performance of the solar cell because of its low hole mobility which is around 5-6 orders of magnitude lower than the HTM using $\text{CuSnI}_{2.95}\text{F}_{0.05}$, but also limited by its low conductivity (1, 12, 13).

Despite the impressive analysis of different ssDSSCs performance with normalized methods for measuring the efficiency and the characteristics, the stability of the ssDSSCs is rarely reported (6). To help ssDSSCs become widespread across the market and investors, the stability of the cells needs to be improved and the missing reports and analysis of the stability does not help the cause (14). The production cost of ssDSSCs is already low compared to other photovoltaic alternatives like perovskite or silicon based solar cells, but it also requires long term stability to further lower the cost and pique the interest of the market (14, 15, 19). Most HTM in ssDSSCs are doped with additives, which has shown to increase the conductivity and efficiency of the cells but comes with disadvantages like charge recombination and incident light filtering (22). These additives also increases the complexity of the cells, which harms the ability to properly analyse mechanisms, optimize performance and mass produce (22). In addition, additives increase the cost of the cells and may cause unknown side reactions leading to worse long-term stability (22).

One of the main causes of cell degradation in a ssDSSC using spiro-OMeTAD as a HTM when exposed to high temperatures is crystallization in the HTM, which could affect the contact between the dye and HTM leading to poor performance (20). A possible solution is the incorporation of extra elements in the structure of the HTM to make it asymmetric (20). Making the molecule asymmetric makes the material less prone to crystallization without changing its properties and different degrees of asymmetry has been researched and reported (20). The HTMs with the most asymmetry, completely replacing one the diphenylamine rings with a triphenylamine group showed lower performance than the original spiro-OMeTAD, with a PCE of 2.2% and 2.1% compared to 4.8% due to the lower J_{sc} most probably caused by increased charge recombination between the dye and HTM from the modifications (20). However, the asymmetric HTM (HTM1) with the least amount of modifications, only adding a methyl group to the meta position of one of the two rings in each of the four side diphenylamine side groups showed identical efficiency as the original and vastly improved stability (14, 20). HTM1 only lost around 10% efficiency after 1000 hours at 60° C compared

to losing almost all efficiency after all the available space became occupied by crystalline domains in the original (20). Another report showed that p-doping Spiro-OMeTAD with FK102 did not have any negative effect for the stability of the ssDSSC, only losing around 20% efficiency after around 1000 hours at 60° C under one sun illumination (16). This loss in efficiency was mostly due to a gradual decrease in FF as the J_{SC} stayed constant and V_{OC} stayed constant after an initial drop of 50 mV (16).

In a previously mentioned HTM, $CsSnI_3$, where Sn is in a 2+ oxidation state, the ssDSSC using this HTM suffered from stability issues caused by the rapid transformation of Sn^{2+} to Sn^{4+} under ambient-air conditions (6, 23, 24). An unencapsulated cell using $CsSnI_3$ showed severe instability issues under 1 sun, ~10% humidity and ~45° C, losing all its efficiency in around 40 hours (24). A method to stabilize the tin based HTM is to use the oxidized Sn^{4+} instead, which is shown to be air-stable (14, 23). Making the compound air-stable reduces the chance of the compound getting hydrolysed during processing and device operation, increasing its stability (21). The ssDSSC using $CsSnI_6$ as a HTM with additives like Li(TFSI) and *t*-BP showed a PCE of 6.32%, which is lower than its $CsSnI_3$ counterpart, but the stability is improved by at least an order of magnitude with the usage a sample cell using the dye Z907 being stable for at least 800 hours without any light soaking other than for data sampling (1, 23).

To produce ssDSSCs without the usage of additional additives in the HTM, single-component electrolytes have been researched and a modified imidazolium ring by an addition of a propargyl group (PMIm) enhanced the conductivity by about 40,000 (22). The cell without any additives had a PCE of 6.3% and showed that the efficiency remained very stable during continuous light soaking under 1 sun illumination for 1500 hours (22).

The stability of the copper based HTM mentioned earlier using a blend of $[Cu(TMBY)_2]^{2+}$ and $[Cu(TMBY)_2]^+$ was reported and after 200 hours of 0.5 sun illumination the cell retained 85% of its original efficiency (3). The stability of another cell using the same HTM, but using a different dye was evaluated at room temperature (4). This cell retained 96% of its original efficiency after 1000 hours, its long shelf life can be due to the methyl group substituents at the 6,6'-positions in the copper complexes which can stabilize the complexes against moisture and oxidation (3).

4. Conclusion and future outlook

Since silicon based solar cells are more efficient, the cost efficiency being less relevant due to reduced prices of silicon based systems and ssDSSCs not showing much improvement in the efficiency under one sun illumination despite multiple decades of research. The best efficiencies recorded for the electrolytes based on imidazolium, CsSnI₃, Spiro-OMeTAD and copper is 6.6%, 8.0%, 8.5%, 11.7%, respectively. Since the improvement of the efficiency of the cells is not improving, it could be better in terms of sales value to focus on harvesting and recycling inside light, where ssDSSCs perform best (14). A possible problem with switching from focusing on efficiency to stability, can be that the interest in improving stability for customers could be lower compared to the interest in improved efficiency. In order for the cells to be incorporated in society as the most prominent solar cells for use indoors, the stability of the cells needs to be improved. While improving the long term stability of low performance ssDSSCs might not seem important, it can however be used to learn different sources which affect the stability and use the knowledge gained in future high performance ssDSSCs. Since research has shown that the use of additives in the HTMs of ssDSSCs can decrease the long-term stability of the cells, focus on single component electrolytes like PMIm can show faster results for improved stability despite not having the highest efficiency. Other alternatives often require additives to achieve its reportedly high efficiencies which can lead to unknown side reactions resulting in lower stability. The materials used in these HTMs however, need to be environmentally friendly, non-toxic, cheap, easily processable and sustainable. Another requirement to expedite the stability of future ssDSSCs is to implement a standard for testing the long term stability, similarly to how efficiency is usually recorded, under one sun illumination. The incorporation of a standardized stability test can make a larger fraction of future reports on new materials include a graph showing its long-term stability and allow for more efficient comparisons between the reports.

References

1. Chung I, Lee B, He JQ, Chang RPH, Kanatzidis MG. All-solid-state dye-sensitized solar cells with high efficiency. *Nature*. 2012;485(7399):486-U94.
2. Saygili Y, Söderberg M, Pellet N, Giordano F, Cao YM, Muñoz-García AB, et al. Copper Bipyridyl Redox Mediators for Dye-Sensitized Solar Cells with High Photovoltage. *J Am Chem Soc*. 2016;138(45):15087-96.
3. Cao Y, Saygili Y, Ummadisingu A, Teuscher J, Luo J, Pellet N, et al. 11% efficiency solid-state dye-sensitized solar cells with copper(II/I) hole transport materials. *Nat Commun*. 2017;8:15390.
4. Zhang WW, Wu YZ, Bahng HW, Cao YM, Yi CY, Saygili Y, et al. Comprehensive control of voltage loss enables 11.7% efficient solid-state dye-sensitized solar cells. *Energy Environ Sci*. 2018;11(7):1779-87.
5. Yella A, Lee HW, Tsao HN, Yi CY, Chandiran AK, Nazeeruddin MK, et al. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science*. 2011;334(6056):629-34.
6. Iftikhar H, Sonai GG, Hashmi SG, Nogueira AF, Lund PD. Progress on Electrolytes Development in Dye-Sensitized Solar Cells. *Materials*. 2019;12(12).
7. Wang H, Zhang X, Gong F, Zhou G, Wang ZS. Novel Ester-Functionalized Solid-State Electrolyte for Highly Efficient All-Solid-State Dye-Sensitized Solar Cells. *Adv Mater*. 2012;24(1):121-+.
8. Mattiello S, Lucarelli G, Calascibetta A, Polastri L, Ghiglietti E, Podapangi SK, et al. Sustainable, Efficient, and Scalable Preparation of Pure and Performing Spiro-OMeTAD for Perovskite Solar Cells. *Acs Sustain Chem Eng*. 2022;10(14):4750-7.
9. Li X, Xu B, Liu P, Hu Y, Kloo L, Hua JL, et al. Molecular engineering of D-A- π -A sensitizers for highly efficient solid-state dye-sensitized solar cells. *J Mater Chem A*. 2017;5(7):3157-66.
10. Shen ZJ, Xu B, Liu P, Hu Y, Yu Y, Ding HR, et al. High performance solid-state dye-sensitized solar cells based on organic blue-colored dyes. *J Mater Chem A*. 2017;5(3):1242-7.
11. Xu B, Gabrielsson E, Safdari M, Cheng M, Hua Y, Tian HN, et al. 1,1,2,2-Tetrachloroethane (TeCA) as a Solvent Additive for Organic Hole Transport Materials and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells. *Adv Energy Mater*. 2015;5(10).

12. Nakka L, Cheng YH, Aberle AG, Lin F. Analytical Review of Spiro-OMeTAD Hole Transport Materials: Paths Toward Stable and Efficient Perovskite Solar Cells. *Adv Energ Sust Res.* 2022;3(8).
13. Xu B, Tian HN, Lin LL, Qian DP, Chen H, Zhang JB, et al. Integrated Design of Organic Hole Transport Materials for Efficient Solid-State Dye-Sensitized Solar Cells. *Adv Energy Mater.* 2015;5(3).
14. Benesperi I, Michaels H, Freitag M. The researcher's guide to solid-state dye-sensitized solar cells. *J Mater Chem C.* 2018;6(44):11903-42.
15. Sharma K, Sharma V, Sharma SS. Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Res Lett.* 2018;13.
16. Burschka J, Dualeh A, Kessler F, Baranoff E, Cevey-Ha NL, Yi CY, et al. Tris(2-(1*H*-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells. *J Am Chem Soc.* 2011;133(45):18042-5.
17. Krüger J, Plass R, Grätzel M, Matthieu HJ. Improvement of the photovoltaic performance of solid-state dye-sensitized device by silver complexation of the sensitizer *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato) ruthenium(II). *Appl Phys Lett.* 2002;81(2):367-9.
18. Wu JH, Lan Z, Lin JM, Huang ML, Huang YF, Fan LQ, Luo GG. Electrolytes in Dye-Sensitized Solar Cells. *Chem Rev.* 2015;115(5):2136-73.
19. Nazeeruddin MK, Baranoff E, Grätzel M. Dye-sensitized solar cells: A brief overview. *Sol Energy.* 2011;85(6):1172-8.
20. Malinauskas T, Tomkute-Luksiene D, Sens R, Daskeviciene M, Send R, Wonneberger H, et al. Enhancing Thermal Stability and Lifetime of Solid-State Dye-Sensitized Solar Cells via Molecular Engineering of the Hole-Transporting Material Spiro-OMeTAD. *Acs Appl Mater Inter.* 2015;7(21):11107-16.
21. Lee B, Krenselewski A, Baik SI, Seidman DN, Chang RPH. Solution processing of air-stable molecular semiconducting iodosalts, Cs₂SnI_{6-x}Br_x, for potential solar cell applications. *Sustain Energ Fuels.* 2017;1(4):710-24.
22. Wang H, Li J, Gong F, Zhou G, Wang ZS. Ionic Conductor with High Conductivity as Single-Component Electrolyte for Efficient Solid-State Dye-Sensitized Solar Cells. *J Am Chem Soc.* 2013;135(34):12627-33.

23. Lee B, Stoumpos CC, Zhou NJ, Hao F, Malliakas C, Yeh CY, et al. Air-Stable Molecular Semiconducting Iodosalts for Solar Cell Applications: Cs_2SnI_6 as a Hole Conductor. *J Am Chem Soc.* 2014;136(43):15379-85.
24. Ye T, Wang K, Hou YC, Yang D, Smith N, Magill B, et al. Ambient-Air-Stable Lead-Free CsSnI_3 Solar Cells with Greater than 7.5% Efficiency. *J Am Chem Soc.* 2021;143(11):4319-28.
25. Alharbi SS, Al Mamun M, Boubaker S, Rizvi SKA. Green finance and renewable energy: A worldwide evidence. *Energ Econ.* 2023;118.
26. Ji JM, Zhou HR, Eom YK, Kim CH, Kim HK. 14.2% Efficiency Dye-Sensitized Solar Cells by Co-sensitizing Novel Thieno[3,2-*b*]indole-Based Organic Dyes with a Promising Porphyrin Sensitizer. *Adv Energy Mater.* 2020;10(15).



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