

Review

A Review on Liquid Electrolyte Stability Issues for Commercialization of Dye-Sensitized Solar Cells (DSSC)

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Abstract: Dye-sensitized solar cells have been under development for the last three decades but are yet to see the market. This has been attributed to stability issues of the electrolyte in the cell. Electrolytes can be liquid, quasi-solid, or solid. Liquid electrolytes were the first to be developed and, therefore, have been subject to radical revisions in both composition and applicability. They have shown the best power conversion efficiencies but have poor thermal stability. Although quasi-solid and solid-state electrolytes were developed to overcome these stability issues, they too have their limits. The aim of this paper is to explore the development of liquid electrolytes, outlining the current state of the technology and considering their potential in the photovoltaic market.

Keywords: dye-sensitized solar cell (DSSC); liquid electrolyte; commercialization; potential; limitations; ionic liquids; organic solvents

1. Introduction

The finite supply of fossil fuels and their adverse effects on the environment have led researchers to investigate various ‘cleaner’ alternatives since the second half of the 20th century. Photovoltaics (PV) emerged as a promising candidate and has been in the market since the early 2000s, amounting to about 945 GW of global installed capacity in 2021 [1]. This includes not only large-scale solar power stations but also small roof-top installations for private use. Most commercially sold photovoltaics are generally either first-generation crystalline silicon cells or second-generation thin-film cells. Both have a relatively high power conversion efficiency (PCE) and service life, which makes them suitable for commercial use [2,3].

Dye-sensitized solar cells (DSSCs) are part of the third generation of PV as they are still in the development stage and are unsuitable for the market at present. However, they offer advantages that might make them more popular than conventional photovoltaic technologies. Unlike these which use silicon or chalcogenide materials, DSSCs can be manufactured with more economical and environmentally friendly components. They also provide the advantage of being semi-transparent and hence customizable as window glass or glass facades for buildings. Moreover, unlike traditional Si-cells, they also have been shown to perform well under dimly lit environments. This makes them ideal for small indoor applications or even building integrated photovoltaic (BIPV) applications that not only generate electrical energy but also add to the aesthetic value [4–6]. At present, however, there are very few DSSCs on the market [7,8].

The problem lies in their low PCE and the instability of several crucial components. Instability issues attributed to the electrolyte are a major contributor to cell degradation and limit the current service life to around 6 years, making them impractical for commercial use. PV modules are anticipated to experience a minimal degradation in PCE of less than 10% compared to their initial efficiency over a span of 20 years of outdoor operation. Moreover, to meet the accepted critical threshold, it is expected that the initial efficiencies should be at least 10%.



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With the energy crisis in Europe and the general need to move towards renewable energies, innovation in PV technology is at an all-time high. In the last decade, there has been a significant increase in the amount of research being conducted and published on DSSCs, providing with them invaluable experimental data. This may finally allow DSSCs to enter the PV market in the foreseeable future. However, there are several technical and non-technical hurdles that it may potentially face. From a commercial point of view, the production costs at the entry stage would probably be higher than those of conventional PV technology. This could deter potential buyers who might find the investment costs too high and the service life too low for a good return on investment. In addition, most consumers are familiar with the blue-tinted glass panels on rooftops, whereas DSSCs would be a completely foreign concept and may not be as readily accepted.

There is currently a growing shift towards a circular economy due to increased awareness of the limited availability of resources [9]. It would be ideal if the market entry of DSSCs is in compliance with circular economy concepts. Ensuring a long life before entering the market would be beneficial not only for economic reasons but also to ensure a sustainable approach to production. In the long run, this would result in lower resource consumption and less waste [10]. In addition to lifetime improvements, other technical factors need to be optimized for DSSCs to be successful in the PV market. It can be argued that because the field of DSSCs is constantly undergoing extensive research and improvement, a consumer may feel the need to frequently replace the product with a “newer and better” version to keep up with developments. This could discourage potential buyers, who may feel the need to wait until the technology is stable enough to invest in it. As a result, this would negate the need for longer lifetimes in the early stages of market introduction but lead to more waste. All the while the extent to which DSSCs can be recycled is largely uncertain. All these factors need to be optimized before the cells can be considered commercially viable.

Among the challenges to enter into the market, the stability issue persists as the most crucial technical aspect, as it also pertains to possible health risks and environmental damage. The composition of the electrolyte is the key to stabilizing the cell; therefore, its analysis could provide a better understanding of the issue and the need for optimization. This paper aims to compare experimental results and theoretical analysis of stability issues found with commonly used liquid electrolytes. The focus would also be on the extent to which these issues are relevant for commercialization.

2. Dye-Sensitized Solar Cell (DSSC)

DSSCs work on the principle of using photosensitive dyes as a medium that captures light energy, which can then be converted to electricity. Although the principle of converting the energy of photons to electricity in this manner was first documented as early as 1972 by Fujishima et al. [11], Grätzel and O’Regan’s work in 1991 enabled the groundbreaking development of DSSCs with notably high efficiency ($\eta = 7\%$) [12]. Their work has since led to much research and advancement with current efficiency values at 15.2% (in laboratory conditions and AM 1.5) as of early 2023 [13].

Design and Working Principles

Figure 1 shows the schematic structure of a DSSC, consisting primarily of two electrodes and an electrolyte in between. The generation of electrons occurs in the photosensitive dye that is administered to the surface of the anode (the working electrode). The most widely used configuration of an anode is that of a transparent conductive oxide (TCO) glass (indium or fluorine-doped tin oxide), coated with a mesoporous metal oxide semiconductor like TiO_2 or ZnO [14]. Titanium dioxide offers a bandgap of about 3.2 eV and is both nontoxic and inexpensive, making it a common choice as the semiconductor material. It is responsible for electron transmission, and therefore, functions better when more of the surface area is exposed. It was the use of the rough surface of a mesoporous layer of TiO_2 instead of a smooth coating that facilitated the breakthrough of Grätzel and

O'Regan in 1991 [3]. A thin film of inorganic or natural photosensitive dye is then adsorbed onto the semiconductor layer of the anode. Cells offer flexibility in the choice of dye used. Panchromatic ruthenium complexes are widely preferred for their high PCE. However, natural plant-based dyes, such as chlorophyll and anthocyanins, are also suitable and offer a less toxic alternative. They, however, tend to have a lower PCE [15]. The cathode is also a TCO glass sheet that encompasses the cell. Between the electrodes is also an electrolyte, a solvent containing a reversible redox mediator (often I^- / I_3^- redox couple).

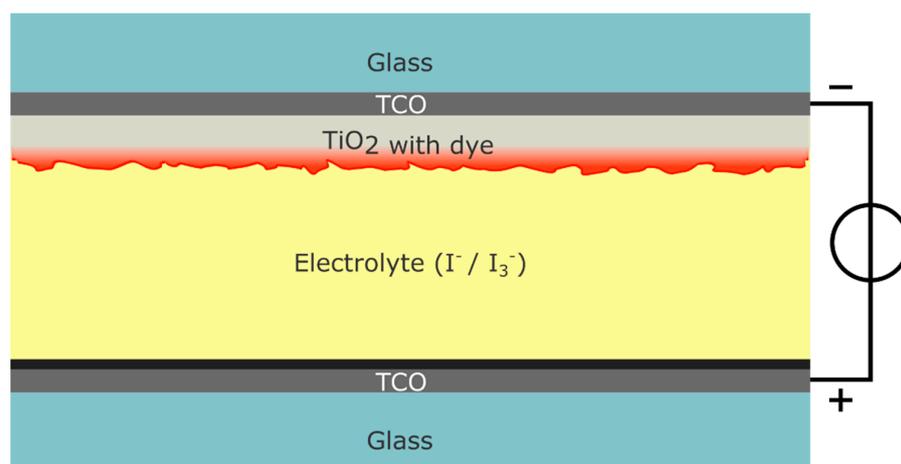


Figure 1. Working principle of a dye-sensitized solar cell. From [16], originally published under a CC BY 4.0 license.

The incident photons oxidize the dye sensitizer from the ground state to the excited state. The sensitizer is then oxidized as the excited electron leaves the LOMO (lowest unoccupied molecular orbital) and enters the conduction band of the metal oxide layer on the anode. The rate of this ‘electron injection’ from the dye to the semiconductor without recombination dictates the efficiency of the cell. The electrolyte’s redox pair is also a crucial component as it supplies the oxidized sensitizer with the electrons necessary to regenerate, thus facilitating better electron injection into the semiconductor by hindering undesirable recombination. The oxidized I_3^- ions then migrate to the counter electrode. Here, they are reduced once again to I^- anions by the electrons that have traveled from the anode through an external circuit, and so the circuit is closed [3,17].

The defining values of a DSSC are the cell’s short circuit current density (J_{SC}), open circuit voltage (V_{OC}), and the fill factor (FF), which is the ratio of the maximum power of the cell to the product of V_{OC} and J_{SC} , from which the power conversion efficiency can be determined. The reactions facilitated by the electrolyte play a crucial role in determining these values, and their behavior over time. Therefore, to enhance the service life for commercialization purposes, cells must be developed with a focus on minimal degradation of the PCE, V_{OC} and J_{SC} values.

V_{OC} depends on the energy difference between the electrons at the anode and those at the cathode [3]. This is the maximum voltage that the cell can supply to an external circuit, and in a DSSC is primarily dependent on the redox potential of the electrolyte (redox pair) and the Fermi level of the semiconductor layer [4]. In an open circuit, the potential at the cathode is equal to the redox potential of the electrolyte, while the potential at the anode is equal to the Fermi level of the semiconductor (e.g., TiO_2). Undesirable reactions between electrons in the anode and the redox couple of the electrolyte can significantly reduce the V_{OC} of the cell. On average, these recombination reactions occur at a much slower rate than the main reaction, but their effects are evident when observed over longer periods of time. This makes it a relevant factor that needs to be limited or eliminated before commercialization [13]. Si-based PVs on the market have an average lifetime of 25 years, which is far beyond what DSSC can offer in its current state [18,19].

Among the various components of a DSSC, the electrolyte has the greatest influence on the long-term stability of the cell. As such, it is arguably the most extensively researched component, with variations in design, composition and shape over the years. Primarily, the electrolyte is chosen so that the recombination of electrons in the metal oxide conduction band with the redox couple is minimal, and that it can withstand external influences (such as temperature differences) without breaking down (chemical stability) or corroding other components [3,17]. As mentioned earlier, it also plays an important role in determining the PCE of a cell. Keeping the PCE as high as possible is a priority, but highly efficient cells tend to be more unstable by nature. This can be seen as a driving force in the search for a type of electrolyte that offers the best compromise.

Organic solvents were among the first electrolytes used. However, they are highly volatile and toxic, which led to the development of cells using ionic liquids such as imidazolium, pyridylium and guanidinium. However, these have to be adapted to overcome the problems of volatility and toxicity while still allowing sufficient ionic conduction. Leakage issues can still occur and sealing methods or the use of quasi-solid or solid electrolytes have been proposed as alternatives.

The two most commonly used types of liquid electrolytes in DSSCs are discussed in the following sections. New types of liquid electrolytes, such as glycerol-based electrolytes, are constantly being explored as alternatives that could overcome the limitations of existing types [20]. Due to the lack of sufficient experimental data on these lesser-known electrolytes, they will not be discussed in detail.

3. Volatile Organic Solvents

The most commonly used form of electrolyte is a solution of an ionic redox couple (such as I^-/I_3^-) dissolved in an organic solvent such as nitriles (organic compounds containing $-C \equiv N$ groups) or esters. The key properties that characterize a solvent are its polarity, viscosity, boiling point and the diffusion coefficient of ions (such as I^- -ions) in the solvent. An ideal solvent should be nonreactive with the dye or semiconducting material. Acetonitrile, the simplest form of nitrile, is the most commonly preferred solvent. As an aprotic solvent, it interacts mainly through dispersion forces [21], rather than readily donating its proton for hydrogen bonding. This ensures that the electrolyte does not interfere with the adsorption of the dye onto the semiconductor layer, as has been seen with protic solvents such as water and alcohols [22,23]. Other solvents that may be used include nitriles such as propionitrile, pentanenitrile or larger nitriles (such as methoxyacetonitrile and 3-methoxypropionitrile) and esters such as ethyl carbonate and polyvinyl carbonate (PC).

The size of the molecule has been found to be closely related to its properties. In general, smaller molecules have shown better PCE values, whereas larger nitrile molecules are more likely to exhibit better stability [24]. This is because smaller molecules are more likely to be less viscous, which allows better charge diffusion but also makes them more susceptible to thermal degradation. Acetonitrile, due to its molecular structure as the simplest nitrile hydrocarbon, has a very low viscosity (0.34 cP at 25 °C, water for comparison has a dynamic viscosity of 0.890 cP at 25 °C) which allows the redox couple to move faster [3]. The low viscosity also allows for the dissolution of additives, which can further enhance the properties of the electrolyte without significantly hindering charge diffusion through increased viscosity. In addition, acetonitrile has a higher apparent diffusion coefficient for I^- ions compared to larger nitriles such as methoxyacetonitrile [24]. Therefore, an iodide-based redox pair can be easily dissolved in it. A wide electrochemical window, which is the difference between its reduction potential and the oxidation potential at which the electrolyte breaks down, ensures that the electrolyte does not easily react with the electrode or undergo degradation [25,26].

Acetonitrile is commercially produced as a by-product of the synthesis of acrylonitrile (propylene ammoxidation) with a yield of 2–4 L per 100 L of acrylonitrile [27,28]. It is widely used in UV spectroscopy, liquid chromatography, and lithium batteries, as well as

in the synthesis of pharmaceutical products such as vitamins and as a solvent for insulin. Compared to other nitriles, acetonitrile is, therefore, the most readily available solvent for a DSSC. Its properties as a solvent, and how to improve them, are constantly being studied, given its many applications. 148.9 kilotons will be produced in 2022 and an estimated 197 kilotons could be produced in 2027 based on current trends [29]. While availability makes acetonitrile the most cost-effective option, issues of leakage and thermal degradation need to be addressed. Certain additives have been found to significantly improve PCE or increase thermal stability. One such additive is 4-tert-butylpyridine (TBP), which has been observed to increase PCE by limiting unwanted charge recombination [30]. These issues and the possible solutions that are currently under consideration will be the subject of further discussion in the sections below.

3.1. Common Issues

3.1.1. Volatility and Thermal Decomposition

Ideally, the solvent should have a boiling point above 100 °C; this would ensure that the solvent does not evaporate at elevated temperatures during operation. However, volatile organic solvents, as the name suggests, are highly volatile, meaning they have lower boiling points and can evaporate easily. Propionitrile has been suggested as an alternative to acetonitrile as it has a higher boiling point (97.2 °C) compared to acetonitrile (81.6 °C) [31,32]. According to the accelerated aging tests carried out by Hinsch et al., thermal stress was found to be the most critical factor, which can be directly attributed to the chemical properties of the electrolyte, (the solvent and the additives) [33]. In the case of thermal decomposition, both acetonitrile and propionitrile give off highly toxic fumes consisting of nitric oxide and cyanide [34]. Leakage can, therefore, be highly hazardous and toxic to the environment, requiring appropriate sealing procedures.

As mentioned above, the volatility of liquid electrolytes could be suppressed by using additives. Yoon et al. carried out a series of tests to model the energy efficiency of a building using DSSCs as building integrated photovoltaics (BIPV) in the form of windows. They used an electrolyte containing lithium iodide, 1-hexyl-2,3-dimethylimidazolium iodide, guanidium thiocyanate and 4-tert-butylpyridine (TBP) additives in a solvent mixture of acetonitrile and pentanenitrile [35]. Guanidium thiocyanate is a popular additive that not only has a positive effect on PCE but also improves thermal stability [36]. TBP, discussed earlier, is highly effective in enhancing PCE and is also used in most studies of liquid electrolyte DSSCs in BIPV [37]. An 85:15 mixture of acetonitrile and pentanenitrile (boiling point: 142 °C), as used by Yoon et al., was found to be less volatile than pure acetonitrile while keeping the viscosity low enough for good charge transport [35,38].

3.1.2. Leakage Issues and Sealing Methods

Liquid electrolytes are highly susceptible to leakage issues, and for toxic solvents like nitriles, this could result in serious health and environmental damage. No product that carries such a risk would be allowed for commercialization, and therefore, appropriate measures must first be adopted. Alternative constructs such as solid-state polymer electrolytes have gained significance due to these issues but, considering higher PCE achievable and estimated lower production cost of liquid electrolytes, it might still be of interest to consider sealing methods.

There are several factors to be considered when choosing an appropriate sealant. The high polarity of organic solvents makes them capable of dissolving most organic compounds. Therefore, the sealant itself might also be in danger of corrosion. Furthermore, the sealant must be able to protect the cell from external influences like moisture and heat. To achieve high-temperature resistance, superior seal integrity is critical [19].

DSSCs need to be sealed in two critical areas of the cell, (1) the edges to encapsulate the cell, and (2) the electrolyte injection holes. The sealant covering the injection holes is highly susceptible to electrolytic corrosion as it is in direct contact with the electrolyte. However, this is not as significant in the case of quasi-solid or solid-state DSSCs. However, the sealant

covering the edges is critical for all types of electrolytes. It must not only prevent leakage but also protect the cell from moisture and other external influences. Thermoplastics, UV-curable resins and glass frits are the most commonly used sealants. While thermoplastics are cost-effective due to their use in other areas, they tend to have a low tolerance to water, oxygen and UV [39]. UV-curable resins have better tolerance and thermal stability but are polymers that often corrode due to the high polarity of the electrolyte. They are, therefore, unsuitable for long-term use, especially at the electrolyte injection holes [40]. The use of silicone rubber or the process of glass frit bonding has been proposed as an alternative to organic sealants due to their high moisture, heat, UV, and electrolyte tolerance [41]. Glass frits in particular provide airtight hermetic encapsulation, but this process generally requires high temperatures of over 300 °C. This is not feasible as components such as the electrolyte cannot withstand such high temperatures. As an alternative, Martins et al. proposed laser-assisted fritting, which is more compatible with other cell components because it uses laser beams that only raise the temperature for a very short time (a few seconds) [42]. Such sealing methods may be the most effective solution, but they are also more expensive than conventional sealants [43]. It may, however, be argued that the increasing market share of laser technology could make the complete sealing of DSSC using laser-assisted glass fritting commercially viable.

Another possibility is shown by Kato et al. [44] who used olefin elastomer, acrylic and epoxy resin, and polyisobutylenes to seal the glass flakes. With further optimization, they were able to produce DSSCs with 75% residual efficiency after 12 years outdoors.

3.1.3. Light Absorption

Another problem with acetonitrile is its absorption in the visible-light spectrum. Accelerated aging tests have identified visible-light absorption, ultraviolet (UV) exposure, and thermal effects as stress factors on the stability of DSSCs [33]. Hereby, it was noted that stress caused by visible light absorption is not as degrading as the other two factors, but still results in a drop in V_{OC} and J_{SC} values. UV exposure, on the other hand, significantly adds to instability. In general, it is not the solvent that is directly affected, but rather the dissolved iodide redox couple. The solvent, however, must be chosen based on its absorption in the UV spectrum. Acetonitrile, which is commonly used in high-power light chromatography, has a relatively low absorption in the UV spectra which enables it to be a good solvent, despite the absorption in the visible light spectrum. It is believed that the irreversible reduction of iodine in the (I^- / I_3^-) redox pair to iodide is the main cause of degradation through UV exposure as it depletes the number of charge carriers. This process is called electrolyte bleaching and is believed to cause discrepancies at the TiO_2 -dye-electrolyte interface (photoactive area). Some studies have suggested that UV exposure might be causing the excitation of the TiO_2 which in turn leads to the oxidation of organic compounds [4]. To combat these issues, the implementation of UV filters has become typical for the design of DSSCs [45,46]. Furthermore, alternatives to TiO_2 and iodide base redox complexes have been explored [4].

The disadvantage of incorporating UV filters would be the additional cost of production. Furthermore, it is uncertain to what extent UV filters actually limit UV degradation in outdoor conditions. Poskela et al. argued that the commonly used UV filter with a cut-off of 400 nm may not be sufficient for outdoor use [45]. The aging test results of DSSCs exposed to visible light only and DSSCs exposed to the full spectrum including UV light (using xenon lamps) with a UV filter were compared. It was found that after 1500 h of exposure, the PCE of the visible-light DSSC remained largely stable, whereas that of the UV-exposed DSSC decreased to 10% of the initial efficiency, despite the UV filter. In order to determine the reason for this degradation, the electrochemical impedance spectra (EIS) of the tested cells were measured. EIS is an impedance measurement made by varying the frequency of an AC power supply. The different components of the cells respond to different frequencies, for example, the impedance of the TCO-coated electrodes approximates that of an ohmic series resistance. The EIS in Figure 2a shows that this value remains more

or less stable for the first 2000 h. Meanwhile, an increase in internal resistance caused by reduced charge transfer (Figure 2b) and diffusion (Figure 2c) contributes immensely to the internal resistance after only 1000 h. This can be explained by the irreversible reduction of iodine. It shows that UV filters may not be sufficient to completely eliminate the adverse effects of UV light on the cell. Choosing a redox pair or electrolytes that do not have the iodide-triiodide redox pair may be a better alternative for longer life.

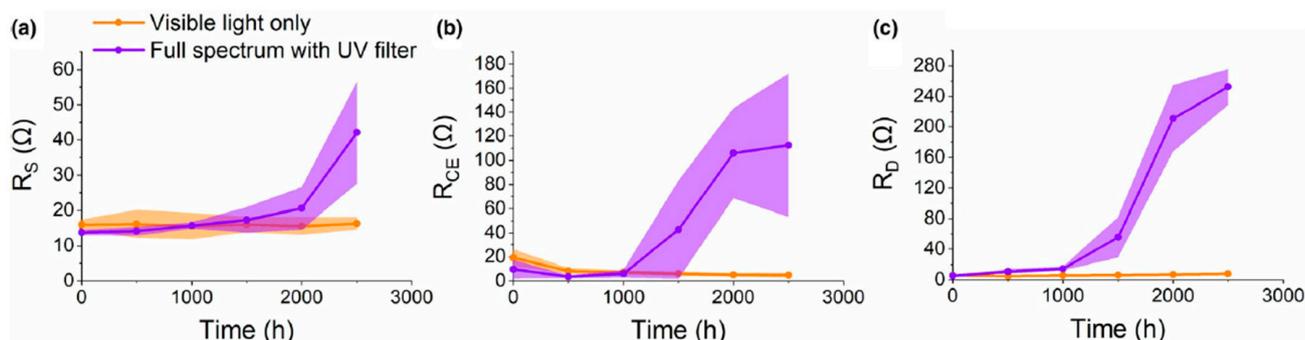


Figure 2. Internal resistance of the cell as seen through Electrochemical Impedance Spectra of (a) ohmic series resistance, (b) charge transfer resistance, and (c) diffusion resistance. Shaded area depicts standard deviation. From [45], originally published under a CC BY 3.0 license.

Such stability tests of DSSCs are often conducted under controlled conditions using lamps that simulate sunlight (such as sulfur lamps or light-emitting diodes (LEDs) for visible light spectra and xenon lamps for the entire light spectrum) to simulate normal conditions. Conclusions drawn from these tests may not necessarily apply to actual outdoor applications. Tests carried out in the actual working environment of DSSCs are still very rare and may be necessary in order to correctly predict PCE values or J_{SC} curves over time.

3.1.4. Instability of Redox Mediator

In addition to the UV-incompatibility of (I^-/I_3^-), it also poses several other problems. Firstly, the iodide-based redox couple could corrode sealant material or metals (like silver and copper) that are employed as electron collectors in large-scale module concepts [47]. As a result of damaged sealant integrity, the risk of iodine vapor leakage could be a serious problem [4]. Moreover, triiodide and other polyiodides (like I_5^-) that may temporarily exist in the solvent absorb part of the visible light spectra competing with the dye and reducing the PCE. The regeneration of the dye as facilitated by the iodide/triiodide system is believed to be a complex two-electron oxidation step process that causes undesirable energy loss and limits the overall achievable V_{oc} [4,47]. In the two-step process the I^- along with the oxidized dye first forms a diiodide radical $I_2^{\cdot-}$ which has more negative redox potential than the (I^-/I_3^-) pair. Therefore, the formation of the radical leads to a loss of energy [48,49]. Other redox mediators include pseudo halogen based $SCN^-/(SCN)_2$ and $SeCN^-/(SeCN)_2$ which have lower redox potentials, this could facilitate lower energy loss during dye regeneration. The $SCN^-/(SCN)_2$ in particular, was observed to have insufficient current densities, and the rate of dye regeneration was considerably lower than that of (I^-/I_3^-) [49,50]. This could be due to lower diffusion coefficients.

Redox complexes are a crucial component of both liquid and gel-based quasi-solid DSSCs. As seen in the case of the iodide-triiodide pair, the redox couple can significantly affect the photovoltaic values of a cell. In general, this depends mostly on their redox potential, which in the case of DSSCs is the driving force for the reduction of the oxidized dye [51]. It is usually described using the Nernst equation as follows:

$$E_{redox} = E_{red}^{\theta'} - \frac{RT}{zF} \ln \frac{a_{red}}{a_{ox}}$$

Here, E_{red}^{θ} is the standard potential measured against a standard hydrogen electrode. (I^-/I_3^-) has a standard potential of 0.35 V, (Co^{3+}/Co^{2+}) 0.56 V and (Cu^+/Cu^{2+}) 0.87 V. 'R' is the gas constant, 'T' the temperature and 'F' is the Faraday constant. 'z' represents the number of electron oxidation steps, which for the (I^-/I_3^-) has a value of 2, whereas (Co^{3+}/Co^{2+}) or (Cu^+/Cu^{2+}) this would be 1. a_{ox} and a_{red} describe the chemical activity of the oxidized and reduced species, respectively [49]. A comparative depiction of the redox potentials of (I^-/I_3^-), (Co^{3+}/Co^{2+}) and (Cu^+/Cu^{2+}) can be seen in Figure 3.

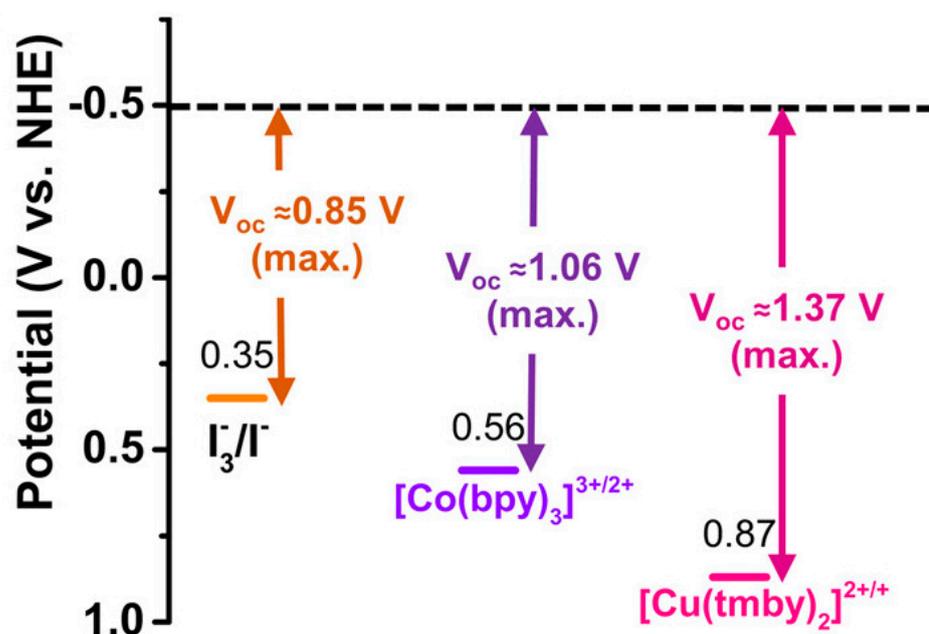


Figure 3. Redox potential of different redox mediators and their theoretical maximum open circuit voltage. From [49], originally published under a CC BY 4.0 license.

The use of transition metal redox complexes has also been proposed as an alternative, including but not limited to cobalt and copper-based pairs. The main advantage of these complexes over halogen-based ones is the tunability of the redox potential. This can be achieved by the selective combination of specific ligands. Nusbaumer et al. suggested that the cobalt complex $[Co(dbip)_2](ClO_4)_2$ has minimal absorption in the visible region. Although they showed exceptional PCE results in low light, this was not the case at high light intensities [52]. The redox complex is susceptible to hindered mass transport due to the larger molecular size, resulting in recombination reactions. [53]. To counteract these problems, the use of appropriate ligands (for example, 2,2'-bipyridine (bpy) as a bidentate ligand) has been proposed. Feldt et al. showed that $[Co(bpy)_3]^{3+/2+}$ when paired with hexafluorophosphate (PF_6^-) counterion had an optimal driving force and good mass transport due to the smaller size of the cobalt complex [54]. With the use of co-sensitized dyes, efficiencies of up to 14.2% have been reported [55]. Copper-based redox couples are also worth mentioning due to their non-toxic nature and lower cost compared to cobalt. Using a copper-based redox couple, Freitag et al., were able to obtain 11.3% PCE at AM of 1.5 G [56].

4. Ionic Liquids

Although organic solvents have shown the best efficiencies, their volatility makes them unsuitable for elevated temperatures. As a result, iodide-based ionic liquids (ILs) have been proposed as an alternative or additive to organic solvents [57,58]. Ionic liquids are essentially salts that are liquid at low temperatures (generally, but not limited to, a melting point of less than 100 °C). Room temperature ionic liquids (RTILs) are liquid at room temperature (around 20 °C to 25 °C). As the name suggests, the liquid is composed

entirely of ions, and the combination of cation and anion can be varied as required, giving them the name ‘designer solvent’, and allowing free choice of properties (such as volatility or polarity).

Due to the large number of possible cation-anion combinations, the classification of ILs is difficult. However, the two types that are most relevant to DSSCs are the halide-based ILs and the heterocyclic ILs. Halide-based ILs showed high thermal stability and were one of the first types to be investigated. However, they break down easily and can form strong acids (such as HCl) when exposed to water [24]. The ionic liquids that are most commonly used for DSSCs are heterocyclic compounds, such as imidazolium salts, with 1-alkyl-3-methylimidazolium as the preferred organic cation [24,59]. These salts are RTILs with good diffusivity and stability. Their relatively wide electrochemical window makes them excellent electrolytes. The viscosity and density of the IL are determined by the length of the alkyl group in the cation. The longer the chain, the higher the viscosity and the lower the density. In general, however, ILs are much more viscous than organic solvents such as acetonitrile, which hinders charge transport and facilitates unwanted recombination reactions. To mitigate this problem, a higher concentration of the redox mediator is required, preferably one that is not iodide based to avoid rapid degradation [60,61]. Much research is also being conducted on their potential as quasi-solid electrolytes in the form of ionic liquid crystals (ILCs). This could potentially eliminate the risk of leakage [62].

A study by Gao et al. compared the aging test results of different electrolytes used in DSSCs (see Table 1). The widely preferred acetonitrile-based electrolyte was found to have high efficiency and the best FF. However, due to the volatility of acetonitrile, long-term thermal tests could not be carried out. This again highlights the need for other types of electrolytes to commercialize DSSCs. They then tested the longer-chain methoxypropionitrile-based electrolyte, which had a lower efficiency but performed well in the thermal aging test. The efficiency dropped to just under 9% after 1000 h of AM 1.5G irradiation at 60 °C. The ionic liquid electrolyte showed a significantly lower initial efficiency, but the device efficiency only decreased from 7.41 to 7.04% after 1000 h, while the other values remained more or less constant [63].

Table 1. Comparison of electrolytes used by Gao et al. and their measured values. From [63].

Electrolyte Used	Short Circuit Current Density $J_{SC}/mA\ cm^{-2}$	Open Circuit Voltage V_{OC}/mV	Fill Factor FF	Efficiency $\eta/\%$
Acetonitrile-based	18.62	744	0.755	10.5
Methoxypropionitrile-based	17.98	746	0.737	9.7
Binary ionic liquid	14.77	681	0.737	7.41

ILs can also be used in combination with an organic solvent or as an additive to an organic solvent [64]. In the form of a mixture or binary solvent, the IL imparts thermal stability to the acetonitrile (or organic solvent), and the low viscosity of the acetonitrile, in turn, allows good charge transport. Tedla et al. compared different proportions of the IL, 1-butyl-3-methylimidazolium bromide (BMIBr), in acetonitrile [60]. It was found that mixtures with more than 30% of IL had a lower PCE value. This could be due to the restricted charge transport that occurs with an increase in viscosity. Aging tests were also carried out over 46 days, which showed that the cells with the binary solvent retained more than 85% of their efficiency (Figure 4), whereas the reference cell, which used only acetonitrile, retained only about 60% of its initial PCE [65]. This conclusion provides a plausible solvent that has both good efficiency and thermal stability.

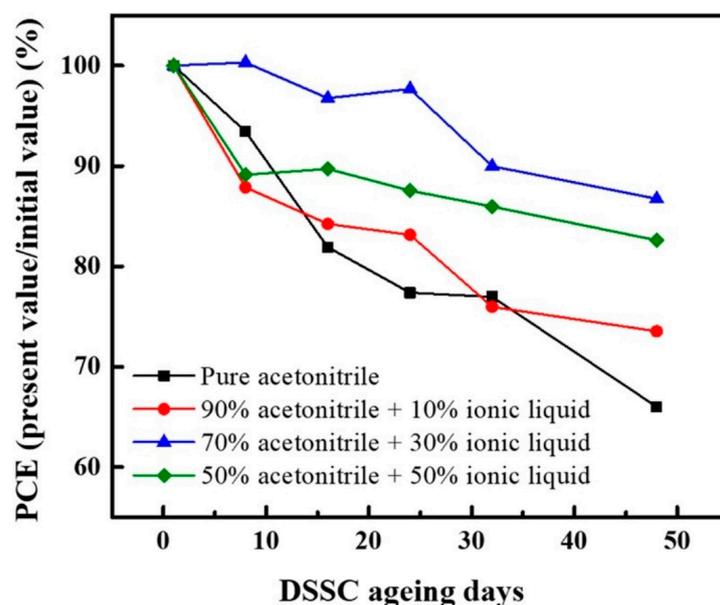


Figure 4. Change in power conversion efficiencies of different concentrations of IL in acetonitrile under aging tests. Reprinted from [65], Copyright (2023), with permission from Elsevier.

The trade-off between efficiency and stability is perhaps the ultimate barrier to DSSC entry into the photovoltaic market. This is where the use of IL additives or binary solvents may be able to provide the balance required for commercial use. There is potential for further developments that could make long-term stability a reality for liquid electrolyte DSSCs. There is also scope for considerable improvement if the other components of the cell (like the dye or TCO-coating) are also optimized. Wang et al. proposed the use of more than one dye sensitizer with an ionic liquid electrolyte to bridge this gap. These co-sensitized systems allow the different dyes to capture a broader spectrum of incident solar light. This opens up the discussion of optimizing other components of the cell to compensate for the loss in efficiency with thermally stable electrolytes. Co-grafting of the dyes C268 and SC-4 on the TiO₂ layer allowed the cell to reach 10% PCE, and after 1000 h of full sun exposure at 60 °C, it showed only a 3% drop in PCE [66].

5. Other Alternatives

Extensive research is also being undertaken in the development of gel-like quasi-solid and solid-state electrolytes. There are several different types of solid-state DSSCs that use either p-type semiconductors, organic hole-transport materials (HTMs), or ionic liquid crystals (ILCs) [67]. The p-type semiconductor-based DSSCs use a p-type semiconductor like Spiro-MeOTAD (2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) or NiO [68,69]. NiO-based cells have shown the best efficiencies but have also been observed to have high rates of undesirable recombination reactions with the dye [70]. Hybrid solid-state DSSCs use organic HTM in combination with an inorganic compound, such as metal oxide. Kim et al. reported a PCE of 6.16% for fiber-based hybrid solid-state cells in 2020 [71]. In general, direct contact with the dye and TiO₂ is hindered by the crystallinity of the solid polymer electrolyte. To overcome this problem, plasticizers can be introduced to reduce the crystallinity and give the electrolyte a more gel-like shape. The increased mobility allows for better ionic conductivity [72]. Polymer electrolytes are by far the best alternatives to volatile organic solvents such as acetonitrile and propionitrile in terms of stability. Furthermore, gel-based DSSCs can be used in textile applications due to their low volatility and non-corrosive properties [73].

Quasi-solid electrolytes have characteristics of both liquid and solid electrolytes. They can be fabricated by incorporating polymers, organic small-molecule gels, or nanoparti-

cles [24]. They have shown better PCE values than solid states due to the ionic conductivity akin to liquid electrolytes, in place of the holes and electrons as charge carriers. Gel polymer electrolyte DSSCs are known for their excellent thermal stability and long-term stability [74]. According to experimental work by Yang et al., the GPE cell retained 83% of its initial PCE after 40 days, whereas the PCE of the reference liquid electrolyte dropped to 27% of its original value [75]. This can conceivably be traced back to insufficient sealing methods or the use of an inadequate electrolyte system (like that of an IL-organic solvent binary solvent). It should be noted that there is a lack of research that directly compares the performance of the best-known Gel Polymer Electrolyte (GPE) cells with equally effective liquid electrolyte combinations. Such comparisons can only be made between different research papers, which might have employed varying methodologies for collecting photovoltaic data. However, since, as pointed out by Wortmann et al. [76], even the comparison of a researcher's results is not always comparable due to lack of reproducibility and slightly varying presentation, we also refrain from such a comparison here. A solution for this problem would be a large series of experiments by a researcher who tries to reproduce the results from different publications under always the same, comparable conditions.

Figure 5 is a schematic representation of four different types of structures in which DSSCs are commonly found. The structure discussed in detail in this paper is shown in Figure 5a, which shows a liquid electrolyte DSSC with a sandwich structure, i.e., two TCO-coated glass plates 'sandwiching' the cell. Although this is the most common configuration, there are other designs that offer various advantages over the sandwich model. Monolithic DSSCs (M-DSSCs) are another common configuration that requires only one TCO-coated glass surface (Figure 5b,c). This could reduce material costs by around 20-30% [77] and allow cells to be easily connected in series to form modules (monolithic serial connection), making them worthy of consideration for commercialization. They could also offer potential advantages in large-scale roll-to-roll manufacturing due to their simplified structure [78]. The use of carbon-based counter-electrodes also makes the cells more cost-effective [79–81]. Figure 5c shows a possible design that eliminates the need for TCO glass and instead uses a Ti-metal back contact coated with a thin compact layer of titanium nitride (TiN). TCO glass is expensive to produce due to the high cost of the raw materials used, the ever-increasing demand and the lack of alternatives. According to a market report by Business Research-insights, the COVID-19 pandemic also saw major disruptions in the supply chain of FTO on a global scale [82], so TCO-free DSSCs may be worth considering for further development.

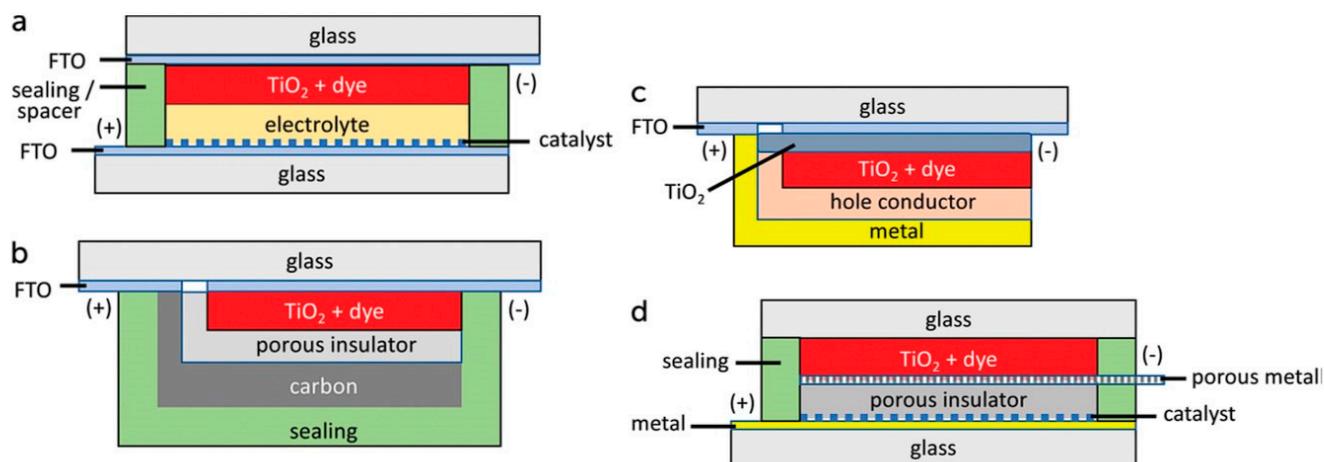


Figure 5. Device structure and components for various proposed DSSC designs: (a) Sandwich cells, (b) monolithic cell with carbon counter electrode, (c) monolithic solid-state cell, (d) conducting glass-free cell. From [4], originally published under a CC BY 3.0 license.

It is also important to recognize our dependence on petroleum-derived compounds. Although optimizing cell efficiency, ensuring high stability and reducing production costs are driving factors in the race to commercialization, this should be accompanied by an awareness of the potential environmental impact. The finite nature of natural resources was the key factor that led to DSSCs and other renewable energy generation methods. Therefore, continued dependence on already depleting non-renewable natural resources must be avoided wherever possible. Research over the last few decades has given us a better understanding of the cell and its components. This should enable us to design components that are sustainable. Various proposals have been made for the use of natural dyes, quasi-solid electrolytes based on biopolymers, natural carbon electrodes, etc. For example, the production of acetonitrile using bioethanol has been proposed by Tripodi et al. as a possible “green” production process for acetonitrile, which, as mentioned above, is in increasing demand from various industries [83]. The simulations carried out show that the use of maize or lignocellulosic residues such as wood and sugar cane as the raw material could help to achieve carbon neutrality and steer the production of DSSCs in an environmentally friendly direction.

6. Conclusions

As mentioned throughout this paper, the compromise between efficiency and stability poses a significant challenge for the integration of liquid electrolyte DSSCs into any market. This challenge has resulted in complexities in cell design and subsequent manufacturing processes. Various aspects, ranging from the preparation of electrolyte solutions to the sealing techniques, have undergone substantial changes in attempts to overcome these challenges. Each type and design of DSSCs come with its own limitations, rendering some more suitable for specific applications than others. Currently, organic liquid electrolytes with ionic liquid (IL) additives and co-sensitized dyes have demonstrated the most favorable balance between efficiency and stability. These configurations show promise as viable designs for large-scale modules. However, achieving such designs necessitates the implementation of appropriate sealing methods. Laser-assisted glass frits have proven to be excellent sealants, although their use may elevate production costs.

In the end, the cost factor will play a pivotal role in determining the feasibility of DSSCs in the photovoltaic (PV) market, particularly as traditional PV technologies become more affordable for consumers. The commercialization of DSSCs as a viable alternative to traditional photovoltaic (PV) technologies holds promise, considering the extensive research and rapid development they have witnessed over the past few decades. While other third-generation solar cells, such as perovskite cells, have emerged as strong competitors to conventional silicon-based PVs, DSSCs may find particular significance in smaller-scale applications, especially considering the growing popularity of the Internet of Things (IoT) and flexible computing technologies. DSSCs uniquely exhibit excellent performance in low indoor lighting conditions, making them well-suited for powering IoT devices and flexible electronics. Additionally, their intricate design and structure can be more effectively implemented in smaller-scale production, aligning with the requirements of these emerging technologies. While perovskite cells may dominate the landscape in terms of overall efficiency and power output, DSSCs offer unique advantages in specific niche applications. Therefore, despite facing competition from other advanced solar cell technologies, DSSCs can carve out a distinct market presence, particularly in areas where their characteristics, such as indoor performance and adaptability to smaller-scale production, align with specific requirements. This would mean that there would be no obligation for the DSSCs to still function profitably after 20 years. Of course, the costs of the cells would have to be calculated differently so that they are already profitable after 5 years, for example. This could be achieved if efficiency-increasing but expensive and difficult-to-handle additives in the electrolyte could be dispensed with and a possible sealing only had to be designed for a quarter of the time. Especially for IoT applications and other niche products that do not require high voltages, simpler DSSC designs could occupy an area previously difficult

to cover by SI-PV and replace batteries and the like here. The saving of mostly toxic additives in the electrolyte and necessary sealing due to the lower requirements for the DSSCs would also directly increase the recyclability. In addition, a stronger focus on a directly well-recyclable construction of the DSSC would be advisable.

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