Overcoming the Mass Transport Limitations of Dye-Sensitised Solar Cells

Towards highly efficient and robust alternative redox mediator electrolyte DSSCs

ROGER JIANG
Dissertation presented at Uppsala University to be publicly examined in Room 2001, Ångström laboratorium, Lägerhyddsvägen 1, Uppsala, Friday, 5 October 2018 at 10:00 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Dr. Frédéric Sauvage (Université de Picardie Jules Verne, Laboratoire de réactivité et chimie des solides).

Abstract

Dye-sensitised solar cells (DSSCs) have been subject to decadelong research interest, and may have some potential niche market applications. Recently, major advances in power conversion efficiencies have been achieved following the transition to cobalt polypyridine based redox mediators. Unfortunately, these champion devices remained unfeasible for commercialisation due to heavy reliance on flammable volatile acetonitrile electrolytes. Overcoming this issue has been a challenge due to increased mass transport limitations, which are especially exacerbated in more stable albeit viscous electrolytes. The overall aim of this thesis is to better understand the contributing factors to mass transport, and then to develop practical solutions to overcome these limitations. In particular, specific mass transport limitations pertaining to the bulk electrolyte medium and electrolyte-infiltrated TiO₂ medium, are investigated. The effect of non-uniform photogeneration profile across the photoanode is explored with respect to mass transport using photocurrent transient techniques. Practical devices engineering for optimal mass transport is explored in terms of minimising the inter-electrode spacing and maximising light absorption towards the electrolyte-electrode side. Alternative devices based on more practical electrolytes with higher viscosity are optimised for high efficiency.

Keywords: Dye-sensitised solar cell, dye-sensitized solar cell, photoelectrochemical cell, cobalt tris(bipyridine), mass transport, photocurrent transients

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urn:nbn:se:uu:diva-357399 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-357399)
To ongoing research into DSSCs

To the hope that our work may some
day be useful to society

To the dream that our scientific en-
deavours may have a meaningful
tangible effect on the world
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  The Impact of Non-Uniform Photogeneration on Mass Transport in Dye-Sensitised Solar Cells

II  Improving the Mass Transport of Copper-Complex Redox Mediators in Dye-Sensitised Solar Cells by Reducing the Inter-Electrode Distance

III Development of high efficiency 100% aqueous cobalt electrolyte dye-sensitised solar cells
Hanna Ellis, Roger Jiang, Sofie Ye, Anders Hagfeldt and Gerrit Boschloo*, Physical Chemistry Chemical Physics, 2016, 18, 8419-8427.

IV  A small electron donor in cobalt complex electrolyte significantly improves efficiency in dye-sensitized solar cells

V  The Effect of Illumination Direction and Temperature on Dye-Sensitized Solar Cells with Viscous Cobalt Complex-Based Electrolytes
Roger Jiang*, Gerrit Boschloo*. Inorganics, 2018, 6(2), 60.

VI  Spatial Photoanode Optimisation for High Efficiency Viscous TPAA/Cobalt Trisbipyridine Complex 3-Methoxypropionitrile Electrolyte Dye-Sensitised Solar Cells

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Contribution Report

Below, I discuss my contributions to the aforementioned papers:

I was the main contributor to **Papers I, V and VI**.

I was a co-author and contributor to **Paper II-III**, with respect to planning, experimental, and write-up. I was responsible for photocurrent transient and MPP stability measurements.

I was a co-author and contributor to **Paper IV**, was I was mainly responsible specifically for MPP measurement experimental (device fabrication) and write-up.
The following list includes publications which I have contributed, however, will not be included in this thesis:

I 2000 Hours Photostability Testing of Dye Sensitised Solar Cells Using a Cobalt Bipyridine Electrolyte

II Chemical and Physical Reduction of High Valence Ni States in Mesoporous NiO Film for Solar Cell Application

III Overcoming the Limitations of Dye-Sensitized Solar Cells

IV The Impact of Reverse Bias on Electrolyte Precipitation in Dye-Sensitised Solar Cells

*corresponding author
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Abbreviations and Symbols

ACN  Acetonitrile
AM1.5G  Air mass 1.5 global
\(c\)  Speed of light
CE  Counter electrode
\([\text{Co(bipy)}_3]^{2+/3+}\)  Cobalt(II/III)tris(2,2’-bipyridyl)
Cheno  Chenodeoxycholic acid
\(\delta_p\)  Depth penetration
D35  \((\text{E})-3-(5-(4-(\text{bis}(2',4'\text{-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid
DB2016  \((\text{E})-3-(5-(4-(4-(4-(\text{bis}(2',4'\text{-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrolo-1-yl)phenyl)furan-2-yl)-2-cyanoacrylic acid
DSSC  Dye-Sensitised Solar Cell
\(e\)  Elementary charge
EE  Electrolyte-electrode
EIS  Electrochemical Impedance Spectroscopy
FF  Fill factor
FTO  Fluorine-doped tin oxide
\(h\)  Planck’s constant
\(I_{\text{peak}}\)  Current maxima in turn-on photocurrent transient
\(J_{\text{SC}}\)  Short-circuit current density (mAcm\(^{-2}\))
\(J_{\text{SS}}\)  Steady-state short-circuit current density (mAcm\(^{-2}\))
\(J-V\)  Current-voltage graph
LEG4  3-{6-{4-[bis(2’,4’-dibutoxybiphenyl-4-yl)amino-]phenyl}-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b’]dithiophene-2-yl}-2-cyanoacrylic acid
MPN  3-methoxypropionitrile
MPP  Maximum power point
PCE  Power conversion efficiency
PEDOT  Poly(3,4-ethylenedioxythiophene)
PV  Photovoltaic (device)
\(Q_{\text{OC}}\)  Charge density extracted from open-circuit
\(Q_{\text{SC}}\)  Charge density extracted from short-circuit
\(R\)  Resistance (Ohms)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_D$</td>
<td>Charge density extracted from short-circuit</td>
</tr>
<tr>
<td>SE</td>
<td>Substrate electrolyte</td>
</tr>
<tr>
<td>$t_{COL}$</td>
<td>Duration of current limitation by electron collection, observed in turn-on photocurrent transient onset</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium dioxide</td>
</tr>
<tr>
<td>TPAA</td>
<td>Tris(4-methoxyphenyl)amine</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>WLED</td>
<td>White light emitting diode</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage (volts)</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zirconium dioxide</td>
</tr>
</tbody>
</table>
Introduction

Before embarking on an in-depth discussion of the dye-sensitised solar cell (DSSC), which is dedicated in the next chapter, broader scope is given on the ongoing challenges for the photovoltaic research field. The impending consequences of climate change are summarised in the popular science section, which is a key motivating reason driving renewable energy research. The aim of this section is to provide a more comprehensive indiscriminate overview of the competitive photovoltaic technologies, whilst providing equal emphasis weighted towards macroeconomic policies, cost efficiency and market competition.

Challenges for Photovoltaic Adoption

We are all partaking in an ongoing world-wide experiment over the long-term effects of greenhouse gas emissions. The concerns over the effects of globally elevated temperatures and environmental impacts of higher CO$_2$, has greatly incentivised politicians to push for more renewable energy research – such as wind, biomass, photovoltaics (PV) and hydroelectric power.

The recent strong growth in especially for PV can largely be attributed to the generous subsidies spearheaded by Germany and China. The introduction of the 2000 Renewable Energy Sources Act (EEG) not only accelerated PV growth in Germany but shaped the PV landscape globally, as similar EEG-derivative policies were adopted by governments world-wide. In essence, feed-in tariffs were used to incentivise active investment in renewable energy source. This guaranteed EEG surcharge payments to investors for contracts of 20 years, primarily determined based on generation and export,$^7$ which substantially eliminated the risk of deflation for early adopters and combined with an attractive return on investment. Multiple iterations of the EEG have since been updated, and more importantly, similar derivatives of the policies have been adopted worldwide by other governments.

Since 2009, the cost of investing in new PV plants in China were heavily slashed through the financing of cheap loans by local Chinese city governments.$^8$ This largely contributed to China’s dominance in PV manufacturing, pushing annualised global PV shipments have been reaching all-time highs, as shown in Figure 1. As of 2017, 98% of all PV shipments were shipped from Asia, with China accounting for 57% of all global supply.$^9$
Most importantly, the average selling price (ASP) for silicon PV modules have continued to decrease exponentially, as shown in Figure 2. The over-saturation of cheap silicon PV modules, especially throughout 2008-2017, has led to global market dominance growing from ~80% to >97%, further cementing its leadership over other PV technologies.\(^9\)

Unfortunately, however, PV energy production remains a small fraction of net energy generation, even in heavily subsidised countries such as Germany where PV accounted for 6.1% of gross energy production in 2017.\(^{10}\) In major countries such as the U.S., solar power accounted for only 1.7% of annual
power generation in 2017. The uptake in PV installations in the U.S., by residential sectors have been almost half that of the entire utility generation sector. To put that in perspective, Figure 3 shows that the U.S. residential sector only accounted for >10% of total energy consumption. Incidentally, industry and transportation sectors are major consumers of power, worldwide. Simply put, there must be a greater uptake of PV energy (or other renewable sources) amongst industry and transportation, in order for any meaningful reduction. The former is more reliant on locally available utility providers, which also requires heavier subsidies to drive renewable energy. Transportation is also a sector which is heavy contributor to global emissions, which remains heavily reliant on petroleum based fuels.

![Figure 3. Historical U.S. total annualized energy consumption by sector. Source: U.S. Energy Information Administration.](image)

**A Zoo of Photovoltaic Technologies**

Photovoltaic (PV) device converts light into electricity through the photoelectric effect, which is a phenomenon that occurs when semiconducting materials are exposed to light. Since the inception of the original selenium P-N junction solar cell in 1873-1876, a multitude of different solar cell technologies have been developed. Most notably, the first silicon PV cell was created in 1954 by Bell laboratories. Most PV devices today operate based on similar mechanisms, where excitons are photogenerated in a light absorbing semiconducting material, which is subsequently separated into charge carriers and extracted to the external circuit, driven by diffusion and electric field. The performance of PV devices can be quantified in terms of its power conversion
efficiency (PCE), describe in subsequent chapters. Generally, for maximal efficiency, PV devices must maximise photogeneration and collection, whilst minimising recombination losses.

Other than cost-efficiency, there are other useful metrics for objectively comparing the environmental impacts of specific photovoltaic technologies. The life-cycle assessment (LCA) becomes an important consideration for more matured and promising photovoltaic technologies, which are attracting industry interest. LCA is used to look beyond the manufacturing costs, and analyses the potential environmental implications resulting from any phase of a product’s life cycle. One common variant is the cradle-to-grave cycle, which looks at the full product cycle such as resources/materials production to the disposal of the product. This can be useful for comparing the advantages or disadvantages of specific photovoltaic technologies, or specific processes. For example, factors to be considered may include:

- the scarcity and ecological/environmental impacts associated with the production/processing of certain raw materials
- the overall energy consumption and potential pollution resulting from manufacturing processes
- the challenges and environmental impact of product recycling or disposal
- quantitative estimates of greenhouse gas emissions for the full cycle

**Silicon and Thin-film Photovoltaics**

Based on the allotropic forms of silicon, this can be further subcategorised, into monocrystalline, polycrystalline and amorphous silicon. Typically, Si-cells are fabricated as a single p-n junction consisting of crystalline silicon. Through doping, the bulk silicon is separated into a p-type and n-type region, which facilitates faster hole and electron extraction, respectively. As of 2018, the state of the art monocrystalline Si-PV devices exceeded 26.7% certified power conversion efficiencies for 79 cm² sized modules. Silicon PV remains unequivocally the most market-dominant and industrially-mature PV technology, based on global market share, scale of government subsidies and competitiveness of cost/watt. Mono- and poly-crystalline silicon PV accounted for ~50 and 45% of global PV shipments in 2017. The cost per watt for silicon PV modules continues to drop below $0.3/W, as shown in Figure 4. In Germany, PV plants deploy commercial silicon based modules with average nominal PCE of ~17% and premium modules exceeding 20%, with production output ranging between 170-200 W per square-meter. Also, the average annualised degradation for silicon PV modules across entire power plants is only averaged 0.1%.

However, silicon is a relatively poor light absorber (compared to some other PV materials), which requires thicker films in order to maximise light harvesting. Also, the purification and production of Si-PV is highly energy
intensive. Finally, the design of Si-PV module is limited to a combination of smaller sub-modules, as opposed to a monolithic thin-film PV, due to the cost of producing larger Si wafers.

Figure 4. Spot price index comparing ASP for various PV-modules. Source: NREL PR-6A20-71493; data from NEF Bloomberg.9

Multi-Junction and Tandem Photovoltaics

Largely in response to the overwhelming cost-competition barrier versus the silicon industry, there is a growing research field with aspirations to combine two or more PV technologies together. This has the end goal of enhancing the efficiency beyond that of individual silicon modules – particularly with regards to the cheaper less efficient amorphous Si-PV modules - by directly stacking additional PV modules with complementary absorption profiles. These so-called tandem devices can be simply connected externally, or monolithically integrated such that consecutive multiple junctions are electrically contacting. The record efficiency for crystalline silicon tandem have been achieved via triple-junction devices (Si/GaAs/GaInP), either mechanically stacking or monolithically, to achieve 35.9 and 33.3% PCE, respectively.16

The state-of-the-art multi-junction PV device based on 5-junction gallium arsenide (GaAs) have exceed PCE of 38.8 %.17 Such multi-junction devices have primarily been deployed for space, where cost effectiveness for power generation is outweighed by the premium for weight. Furthermore, even higher efficiencies in excess of 46 % PCE can be achieved for these multi-junction devices, under concentrated light. Such applications, add even more cost in terms of light concentrating optics and mechanical dual-axis tracking.
Figure 5. Timeline of record certified power conversion efficiencies for various photovoltaic technologies, published by NREL as of 16th Jul 2018.
Emerging Photovoltaics: Organic and Perovskite Photovoltaics

A number of emerging photovoltaics technologies have been gaining research interest, as shown in Figure 6. Prior to heavy government subsidisation of silicon PV industry, the initial incentives driving these fields were to further cut down the production costs associated. There has also been great interest in developing solution-processable solar cells, which translates can present more cost-effective high throughput fabrication, which lower start-up and running costs. Other beneficial niche applications such as semi-transparency and flexible modules have been pursued.

As the namesake suggests, OPV devices usually consist of organic semiconducting polymers. The most successful architecture is currently based on a bulk hetero-junction of P3HT polymer and PCBM fullerene - which corresponds the hole and electron transporting material, respectively. Typically, this is processed from solution, for instance via spin-coating. The best OPV devices rely on a blend architecture in order to increases the interfacial surface area interconnecting these materials, which reduces the average exciton diffusion to the interface. This also highlights the challenges for improving OPV efficiencies, which is that recombination needs to be minimised.

At the time of writing this thesis, the hottest topic is without doubt the lead halide perovskite solar cell (PSC), with certified PCE presently exceeding 20.9 %. The generalised perovskite moniker pertains to the ABX$_3$ cubic crystal structure, where A, B and X can represent an atom or small molecule. This represents a very broad class of crystal structures, with seemingly limitless
possible variations. However, the lead halide derivatives have become of great interest specific to the photovoltaic research field, where the crystal structure usually corresponds to a cation, metal and halide. Funnily enough, the lead halide perovskite structure was initially introduced as a sensitisier for a liquid-junction DSSC,\textsuperscript{19} with disastrous bad stability due to its rapid desorption into the electrolyte – a somewhat important observation absent from the manuscript – which was eventually acknowledged in another work.\textsuperscript{20} Nonetheless, a viable proof-of-concept was demonstrated once a solid-state hole transporting material was incorporated into the device, replacing the electrolyte, reaching efficiencies of 10.9 %.\textsuperscript{21} Sometime later, it was discovered that the perovskite material has both an intrinsically high hole and electron transport mobility, and actually does not require sensitisation of TiO\textsubscript{2} in order to extract electrons.\textsuperscript{22} This led to a somewhat controversial renunciation of the DSSC branding and the subsequent reclassification into a separate category of solar cells.

The toxicity of lead poses a major drawback to PSCs, and presently restricted from being sold in certain markets. EU member states are required to comply with the RoHS 1 directive, which restricts the use of certain toxic materials, such as lead, in electronic household devices.\textsuperscript{23} However, this may simply be a temporary roadblock given the recency of PSCs, and the fact that cadmium based PVs have been previously granted an exception from RoHS 1.\textsuperscript{24}

**Aims of the Thesis**

A significant problem facing DSSCs is that all champion devices are entirely reliant on volatile flammable toxic acetonitrile solvents, undeniably impractical for commercialisation. Despite, the significant recent advancements in laboratory fabricated small module efficiencies, much of these principles remain disconnected for devices specifically optimised for maximal efficiency – such as viscous 3-methoxypropionitrile and ionic liquid based electrolyte DSSCs. The increased viscosity of these more stable electrolyte system is a major factor that limits device performance. The work in this thesis seeks to bridge this disconnect, by seeking strategies to overcome mass transport limitations. Specifically, the work aims to provide better understanding of the contributing factors leading to mass transport limitations, as well as, developing practical strategies for overcoming these issues.
Dye-Sensitised Solar Cells

This section is tailored to provide a broader outline of the key developments in dye-sensitised solar cell (DSSC) research. The information is presented as a series of practical guidelines for each DSSC component, with specific requirements for achieving stable and efficient devices. The aim is to provide the necessary background information, whilst providing practical suggestions, for both newcomers and experts of the subject.

DSSCs have some unique properties that may allow it to succeed in a niche market. This includes properties such as flexible form factors, semi-transparency, colour-tuneability, and higher performance under lower light conditions. As such, DSSCs may be especially suitable for indoor and building-integrated applications, owing to its attractive appearance and superior performance under ambient light.

DSSC Photogeneration mechanism

Photogeneration in DSSCs is driven by light absorption via the dye sensitisier molecule, which injects the electron into the semiconductor. The electron is collected through the semiconductor and extracted to the external circuit. The oxidised dye is subsequently regenerated by via electrolytic redox couple, which carries the positive charge via electrolytic mass transport to counter electrode where it can be reduced. However, loss mechanisms can occur via the recombination of electrons in TiO₂ back to the oxidised dye or oxidised redox mediator. The photogeneration mechanism for DSSCs is unique compared amongst other PV technologies in several ways. Based on current understanding, electron transport predominantly occurs via trap-limited diffusion, as opposed to drift. The high electrolytic ionic strength shields electrons from any substantial built-in electric fields, minimising the effect of drift on overall electron collection. Also, unlike other excitonic solar cells, there no mobile excitons, due to femtosecond timescale electron injection lead to ultrafast charge separation. The work in this thesis is primarily is focused on studying the effects of mass transport, which also happens to be the slowest process kinetic in DSSC, ranging in the ms – s timescale. In particular, current limitations may arise due to the insufficient mass transport of oxidised redox
species reaching the CE, which limit the overall device current output, resulting in a “mass transport limitation”. Also, the mitigation of electron-electrolyte recombination is an especially key issue, present throughout the works.

Dye Sensitiser

The development of panchromatic organic dye-sensitisers with higher molar extinction coefficients, has been especially important for reducing overall photoanode thicknesses required for sufficient light harvesting. Furthermore, a number of important requirements are necessary in order for this to occur:

- the dye, or combination of dyes, should exhibit broad light absorption in order to maximise light harvesting.\textsuperscript{25–27}
- the rate of electron injection from the dye to the semiconductor conduction band (CB) needs greatly exceed that of electron relaxation to the dye ground state.
- the dye must remain firmly anchored to the semiconductor, to avoid desorption into the electrolyte. Ideally, the dye requires an anchoring group with a strong binding coefficient, which also does not negatively affect dye-injection kinetics.
- the dye must remain photochemically and electrochemically inert, especially whilst in the oxidised form. The expected turnover number for the sensitisier lifecycle is directly proportional to the lifetime of its oxidised state, and inversely proportional to the average regeneration time.\textsuperscript{28}
- particularly for one-electron redox mediators, which tend to have faster electron back recombination kinetics, the dye structure needs to include long alkyl chains in order to retard recombination.\textsuperscript{29,30}

The sensitisation of TiO\textsubscript{2} films is usually carried out via immersion in a dye bath solution. A large number of studies have optimised the parameters to promote maximal dye loading onto the TiO\textsubscript{2} substrates, including such factors as temperature, concentration, immersion time, binary solvent mixtures and additional non-light absorbing co-absorbents. The addition co-sensitisation with chenodeoxycholic acid or a similar derivative, has been found to greatly reduce dye aggregation, albeit at the cost of sacrificing increased adsorption of the dye.

\textit{Figure 7} shows the molecular structures of the organic dye-sensitisers used in Papers I-VI, which are based on a donor-π-accepter system, consisting of an electron rich triphenylamine core, linked via a π-conjugated system to an electron deficient carboxylic acid anchoring group. Modifications with respect to the truncated alkyl chains and functionalised π-conjugated systems, have been used to tune the structural and electronic properties of the sensitisers.\textsuperscript{31}
Figure 7. Chemical structures of various organic dye-sensitiser molecules used throughout Papers I-VI, LEG4, D51, D35 and DB2016.
Mesoporous Semiconductor

Prior to 1991, the efficiency of DSSCs were extremely subpar since the devices relied on smooth monocrystalline semiconductors, with low surface area for dye-absorption which severely limited light absorption. This dramatically changed following the introduction of a mesoporous nanostructured TiO$_2$ structure, which led to a 780-fold increase in surface area for dye-loading. Further enhancement of the surface roughness was achieved through titanium tetrachloride (TiCl$_4$) chemical bath treatment, which grows additional metal oxide layer. The addition of larger TiO$_2$ nanoparticles (>300 nm) was later incorporated to induce light back-scattering in order to further enhance the overall light absorption.

The successive deposition of additional ultrathin layers of metal oxide layers, such as aluminium and magnesium oxides, have been investigated to modify dye-coverage or retard electron-electrolyte recombination. For high performance devices, an additional final light scattering layer, consisting of larger TiO$_2$ nanoparticles with sizes up to 400nm, is deposited as a final layer.

An additional pin-hole free compact TiO$_2$ layer deposited onto the conducting oxide substrate has been shown to greatly suppress electron-electrolyte recombination. Devices with more severe recombination typically require denser compact layers, typically prepared via spray pyrolysis.

Some ideal characteristics for mesoscopic semiconductors include:
- exhibit sufficient high mechanical strength to prevent complete detachment of films into the electrolyte.
- have a sufficiently high surface area for maximal dye-absorption, and maximal contact with the electrolyte for optimal regeneration
- have sufficiently large porous voids to allow unimpeded diffusion of the redox mediators
- have a higher conduction band, relative the oxidation potential of the redox mediator, increases the possible attained open-circuit voltages.
- Exhibit maximal transmission with minimal scattering of light, for layers intended for maximal light absorption in the DSSC device.
- For light scattering layers, a greater portion of larger nanoparticles is used for maximal light scattering.

Electrolyte

In liquid-junction DSSCs, charge transport is facilitated by a redox couple in the electrolyte, which simultaneously fulfils the roles of dye regeneration and hole transport. The electrolyte consists of several key components including the solvent, redox mediators and additives, which must each fulfil a set of criterion, in order to coexist compatibly.
Solvent

Despite seemingly trivial, the choice of solvent for the electrolyte is an especially critical component that greatly influences much of the operating processes and long-term stability. The ideal characteristics for the solvent are listed below:

- The solvent must remain electrochemically stable and chemically inert under expected operating conditions.
- The electrolyte solvent must be sufficiently solubilising such that the main electrolytic components, including the redox mediator and additives, can remain completely soluble within the expected operating temperature range.
- The electrolyte solvent should not be too solubilising for the dye sensitisers and catalytic materials on counter electrode, to prevent desorption into the electrolyte.
- With respect to the mechanical stability of electrolyte leakage, the electrolyte solvent should exhibit a sufficiently high boiling point and heat capacity, and exert a low vapour pressure. It also should be noted the density and
- The electrolyte solvent needs to be sufficiently wet and infiltrate into the mesoporous TiO₂ semiconductor. Essentially, there needs to be compatible hydrophobicity between the electrolyte and semiconductor surface. Aside from the solvent polarity, this can also be largely affected by the functional groups of the dye molecule, and electrolyte additives.
- The electrolyte solvent should ideally be cheap, non-flammable, environmentally friendly and non-toxic. The latter is unfortunately limited by the sparse selection of compatible organic solvents. The vast majority of electrolyte solvents are nitrile-based, which tend to be readily metabolised by the human body into hydrogen cyanide – a highly deadly compound. Also, in the EU, ACN has been banned from consumer products due to its toxicity.42

For comparison, a list of commonly used electrolyte solvents are compared below.

Table 1. Comparison of electrolyte solvent properties at 25°C. LD₅₀ oral toxicity for rats.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Vapour pressure (Torr)</th>
<th>Density (g/mol)</th>
<th>b.p. (°C)</th>
<th>f.p. (°C)</th>
<th>Dyn. Viscosity (mPa.s)</th>
<th>LD₅₀ (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>70.7</td>
<td>0.777</td>
<td>81.3</td>
<td>2</td>
<td>0.34</td>
<td>2000</td>
</tr>
<tr>
<td>Water</td>
<td>14.95</td>
<td>0.997</td>
<td>100</td>
<td>-</td>
<td>0.89</td>
<td>-</td>
</tr>
<tr>
<td>3-methoxypropionitrile</td>
<td>1.45</td>
<td>0.934</td>
<td>165</td>
<td>66</td>
<td>1.1</td>
<td>4390</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>37.4</td>
<td>0.772</td>
<td>96</td>
<td>6</td>
<td>0.41</td>
<td>39</td>
</tr>
</tbody>
</table>
All high efficiency DSSCs have been limited to acetonitrile based electrolytes, which are extremely impractical for commercialisation due to its high volatility. As such, alternative solvents for electrolytes were investigated. Water-based electrolyte DSSCs were investigated in Paper III. 3-Methoxypropionitrile-based DSSCs were investigated in Papers V-VI. The properties of several solvents commonly used in DSSCs is listed in Table 1. Unsurprisingly, all nitrile based solvents are highly toxic, since it is readily metabolised in to hydrogen cyanide - where lower LD50 is worse – for instance, propionitrile (PN) is over 100 times more toxic than 3-methoxypropionitrile (MPN). The placebo improvement in volatility for PN over ACN is larger countered by significantly greater toxicity. For that reason, PN was deliberately excluded from further work.

**Redox Mediator**

Ideally, the redox mediator should exhibit the following characteristics:
- remain photochemically and electrochemically inert. A major shortcomings of iodide/triiodide is its corrosive properties.
- highly soluble in the electrolyte, for both the redox mediator and its counterion.
- rapidly regenerating the oxidised dye, with regeneration time constant far exceeding the lifetime of the oxidised dye.
- sufficiently high oxidation potential whilst providing sufficient driving force for regeneration.
- exhibit sufficient overall mass transport.
- exhibit minimal light absorption, in order to minimise competitive light absorption with the dye-sensitiser, especially for EE-side operation.
- exhibit minimal back recombination with electrons in the TiO₂ film.
- having a chemically alterable structure, unlike monolithic iodide redox mediators, may allow the tuning of oxidation potentials to better match different dyes. Cobalt polypyrrole complexes can be modified relatively easily by substituting different ligands.

![Chemical structures of various cobalt polypyrrole complexes used throughout Papers I-VI, shown without counterions which may include Cl⁻, PF₆⁻ and B(CN)₄⁻.](image)

*Figure 8. Chemical structures of various cobalt polypyrrole complexes used throughout Papers I-VI, shown without counterions which may include Cl⁻, PF₆⁻ and B(CN)₄⁻.*
Additives and Other Components

A number of important performance enhancing additives are included in the electrolyte. In general, these cations or bases adsorb onto the TiO$_2$ surface, modifying the surface charge of TiO$_2$, shifting the TiO$_2$ conduction band up and down, respectively. The best performance is usually attained from a combination of both, which usually consists of a lithium ion salt, and 4-tertbutylpyridine.$^{35,45}$

In addition, gelling agents and binary solvent mixtures have been used to decrease the volatility of the electrolyte, in an attempt to improve long-term stability. In some cases, where co-absorbers are loaded onto the TiO$_2$ films, these molecules are also added as additives into the electrolyte to improve the dye-anchoring stability. The most notable example being chenodeoxycholic acid, which has been shown to be a useful co-absorbent that reduces dye-aggregation and promotes wetting of more polar solvents.$^{3,46,47}$

Counter Electrode and Sealing Methods

Typically, a catalytic material is required for the reduction of the redox species at the counter electrode. The most commonly used material is platinum, which is typically deposited onto the substrate via thermally decomposition.$^{48}$ A number of useful attributes for the counter electrode includes:

- The catalyst must remain mechanically attached onto the counter electrode and not mix into the electrolyte.
- The catalyst must remain electrochemically and chemically inert under typical operating conditions.
- The catalyst should be weakly absorbing in light, in order to allow for device operation under back-side or electrolyte-electrode illumination.
- A higher roughness and surface area of the catalyst can promote reduce the charge transfer resistance.$^{49}$
- Ideally, the catalyst should be easily deposited onto the substrate, for instance, without the need for high temperature sintering which is both energy intensive and eliminates compatibility with alternative substrates such as plastics.
- Ideally, the catalyst should be inexpensive, non-toxic and environmentally friendly.

The standard DSSC architecture consists of a two-electrode sandwich separated by an insulating spacer, which simultaneously binds and contains the electrolyte. The most commonly used spacer is DuPont Surlyn 1702, which is a co-polymer thermoplastic consisting of ethylene and methacrylic acid. More recently, this has become commercially available as processed laminate sheets with thicknesses ranging from 50, 25 and 15 µm. It also provides a relatively
fast and low temperature (~120 °C) hermetic seal. Nevertheless, it has been reported that permeability to oxygen and humidity worsens at elevated temperatures.\textsuperscript{50} Other alternative binding materials have been reported in the literature which includes higher melting point thermoplastics (i.e. Bynel), glass frit beads, 2-part epoxy resin and UV-curable polymer resin.\textsuperscript{50,51} Favourable attributes for the sealing gasket material includes:

- The spacer should provide a hermetic seal which simultaneously contains the electrolyte, whilst preventing the ingress of water and oxygen from the outside.

- The spacer should be mechanically robust seal, capable of various forms of stress such as shear, bending and compression. Mechanical failures in sealing greatly increases the chances of electrolyte leakage, which can critically affect device performance.

- The spacer material should be readily processable to uniform sub-micrometre thicknesses.

- The spacer material should have a smaller thermal expansion coefficient.

- Ideally, the processing method for the spacer can avoid higher temperatures, chemical reactions, prolonged exposure to air or UV-illumination, in order to prevent side-reactions with the exposed DSSC components.
Experimental

Device Fabrication
The standard procedure for fabricating DSSC modules is outlined below. However, various modifications to the procedure are implemented Papers I-VI, in order to further optimise mass transport. These details are discussed in further detail in the results and discussion section.

The devices are typically fabricated using fluorine-doped tin oxide (FTO) glass substrates (TEC15, Pilkington, UK), which is thoroughly cleaned using an ultra-sonic bath, immersed in a sequence of detergent, de-ionised water, acetone, isopropanol and ethanol. Platinised counter-electrodes are prepared by drop-casting chloroplatinic solution in ethanol (4µL, 5mM) onto cleaned FTO substrates. For the working electrode, an initial compact pin-hole free TiO₂ blocking layer is deposited onto the FTO substrates via chemical bath treatment in titanium tetrachloride (40mM in water, 70 °C, 90 mins), which is then rinsed in water.

![Figure 9. Sintering of squeegeed TiO₂ films prepared via successive layers deposited via screen printing.](image)

Next, colloidal suspensions of TiO₂ paste (DSL18NR-T, DSL30NR-D, Dyesol, Australia) are squeegeed onto the substrates using a screen printer. After
each deposition, the substrates are briefly heated at 120 °C before any successive layers are applied. Finally, the substrates are heated using a gradated heating sequence with successive heat ramps of 60 mins, rising from room temperature to 180 °C to 320 °C to 390 °C to 500 °C, whilst remaining at each temperature for 30 mins. After gradually cooling the substrates down to room temperature, the substrates are treated once more with a titanium tetrachloride bath treatment, this time for 30 mins. Finally, after rinsing with water and drying in air, the substrates are reheated to 500 °C. After gradually cooling down to 120 °C, the electrodes are immersed in a dye-bath solution overnight. Prior to assembling the devices, the substrates are rinsed with acetonitrile. The counter electrode and working electrode are sandwiched together using a thermoplastic spacer (Solaronix) via a hot-press (Heptachroma) applying 125 °C and 0.2 bar. Finally, the electrolyte is introduced through a pre-drilled hole on the counter electrode, which is then sealed using a pre-cut Surlyn thermoplastic frame and a cover glass.

**Standardised Performance Comparison**

![Graph showing AM0 and AM1.5G solar irradiance spectrum](image)

*Figure 10. The AM0 and AM1.5G solar irradiance spectrum. Reference data obtained from the American Society for Testing and Materials (ASTM) G-173-03 tables provided by NREL.*

For standardised comparisons of photoactive devices, measurements are typically carried out using a light source calibrated to simulate a reference solar irradiance spectrum, as shown in *Figure 10*. Typical terrestrial devices are compared under 1000 Wm$^{-2}$ AM1.5G, corresponding to the area normalised radiant output, and mean free path length for sunlight travelling through the atmosphere, respectively.
Current-Voltage
The current-voltage ($J-V$) measurement is a common method used to characterise the efficiency of a photovoltaic device. Typically, the measurement is carried out with a light source.

$$\eta(\%) = \frac{P_{out}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}}$$

Where $\eta$ is the power conversion efficiency or PCE ($\%$), $J_{SC}$ is the short-circuit current density, $V_{OC}$ is the open-circuit voltage potential, $FF$ is the fill-factor.

$J-V$s are typically measured via linear sweep voltammetry by applying a step-wise increment in voltage, for a pre-defined voltage range.

Several important parameters need to be calibrated for the accurate determination of PCE via $J-V$ measurement. Firstly, the linear sweep scan rate (in volts per second, Vs$^{-1}$) and the incremental voltage step must sufficiently match the RC time-constant of the solar cell. In general, a slower scan rate with a smaller voltage increment should yield more accurate.

Importantly, the sampling delay needs to sufficiently exceed the time-constant of the device, in order to avoid artefacts arising in the measurement – such as $J-V$ hysteresis. This is especially problematic for DSSC which tend to respond much slower to step-wise changes in voltage, as compared to standard silicon PV device.\textsuperscript{52,53}

MPP Tracking
Maximum power-point (MPP) tracking is a measurement technique typically used to determine the maximum stabilised power output of a photovoltaic system, over a period of time. MPP tracking can be especially useful for: 1) the accurate assessment of the power conversion efficiency (PCE), 2) long-term tracking of the device stability under a continuous illumination conditions, and 3) real-time load-balancing for an array of modules operating in fluctuating real-world conditions.

MPP tracking was carried out for \textbf{Papers III-V}, by using an independently custom designed hardware and programmed interface in IGOR Pro. For long-term tracking, a DAQ board was used to potentiostatically maintain multiple devices at MPP. A multiplexer was used to periodically cycle through each device and determine the MPP voltage using a perturb-and-observe hill-climbing algorithm. Essentially, the algorithm applies a series of guess values for MPP voltage, and adjusts accordingly whether power output increases or decreases.
Incident Photon-to-Current Efficiency

The incident photon-to-current efficiency (IPCE), also known as the external quantum efficiency, is a technique used to characterise the conversion efficiency of a given wavelength of light into electrical current. Typically, the IPCE is measured by irradiating the solar device with monochromatic light, with a known photon flux density calibrated using a photodetector, whilst measuring the current output at each given wavelength. The IPCE spectrum can be especially useful for determining the degree of spectral mismatch between AM1.5G relative to other light sources, which significantly affect the perceived performance of devices.

\[
IPCE(\lambda) = \frac{J_{SC}(\lambda)}{e \cdot \varphi(\lambda)} = \frac{hc}{\lambda} \cdot \frac{J_{SC}(\lambda)}{e \cdot P_{in}(\lambda)}
\]

where \(J_{SC}\) is the short-circuit current density, \(e\) is the elementary charge of an electron, \(\varphi\) is the photon flux, \(h\) is the Planck constant, \(c\) is the speed of light, \(P_{in}\) is the intensity of incoming photons, and \(\lambda\) is the wavelength.

In some cases, the IPCE current can be too low to detect due to the low intensity of monochromatic light or the poor IPCE response of the device. In such cases, the IPCE signal-to-noise can be enhanced through the addition of light chopper synchronised to a lock-in-amplifier.

Generally, DSSCs are unstable with respect to UV-irradiance, due to the highly catalytic properties of TiO₂ and potential chemical side-reactions with
electrolyte and dye components. Thus, most practical DSSC would be expected to have a UV cutoff filter attached to external modules.

Assuming the solar cell device does not have current limitations that worsen with light intensity, the IPCE spectrum can be integrated to estimate $J_{sc}$.

$$J_{sc} = \int e \cdot IPCE(\lambda) \cdot I_s(\lambda) \cdot d\lambda$$

where $I_s$ is the absolute irradiance of the light source (typically AM1.5G) that is illuminating the solar cell. For comparison, Figure 12 compares the absorption of a typical LEG4-sensitised DSSC and the spectral irradiance of various light sources.

![Figure 12. Comparison of UV-Vis absorption for a LEG4-sensitised DSSC and the spectral irradiance of various light sources, and including band-pass filters.](image)

### Other Device Characterisation Methods

A brief description of key characterisation techniques is outlined here. Optoelectronic transients and MPP testing instrumentation were independently designed, programmed and hand-built.
Optoelectronic Photocurrent Transients

A typical acquisition sequence for an optoelectronic transient measurement is illustrated in Figure 13. The larger perturbation photocurrent transients have been used to analyse current limitations and recombination. The data acquisition (DAQ) board (NI-6211, National Instruments) was used to synchronise the measurement to the output of a WLED (BXRC-27G10K0-L-03, Bridgelux). The light intensity was further concentrated using an aspheric fresnel lens. The WLED is connected in series with a power MOSFET connected to a programmable power supply. Bi-directional switches were made by assembling two power-MOSFETs in series, which enabled rectification in both directions. The maximum acquisition interval resolution of the DAQ is 4 µs, which is sufficient to observe electron diffusion and electron-electrolyte back recombination reactions. Typically, a longer acquisition interval (>40 µs) is used to allow for more averaging and improve the signal-to-noise ratio. Timing of the data acquisition and light switching is synchronised via the on-board DAQ n-s timer, and power MOSFET with ultrafast switching time; both the DAQ clock and switching time are orders of magnitude faster than the maximum data acquisition resolution for the DAQ. The power MOSFET bridges the connection from WLED to the powers, and is synchronised to a pre-defined pulse train via a digital voltage output from the DAQ. A typical pulse train sequence is illustrated in Figure 13a. A custom software interface was developed in IGOR Pro, in order to automate the acquisition, analysis and plotting of the optoelectronic measurements. Small perturbations in optical intensity was applied via square wave modulations in PSU output, typically ranging between 1-5% in optical intensity. Additional switches were used for
short-circuiting or disconnecting cells. Bias potentials were applied potentiostatically via DAQ. Measurements of current were determined from a differential voltage measured across a resistor relative to ground. Sample holders were designed and hand built from nylon set screws, metal springs, copper sheets and wire. Spring loaded copper contacts were used to simultaneously fix the cell (including in vertical orientations), whilst providing Ohmic contact.

Figure 14. Optoelectronic transient measurement setup (left) and automated stability testing setup (right).

Figure 15. Custom IGOR Pro user interface for optoelectronic measurement data acquisition and analysis. Some of the UI interfaces for $J V$, MPP tracking, oscilloscope.
Photocurrent Turn-on Transients
As shown in Figure 13c, photocurrent turn-on transients are very simple and quick for determining the presence of current limitations in a solar cell device. Sub-linear deviations in the stabilised photocurrent output versus light intensity can indicate a current limiting process in the device. Typically, the interpretation of large perturbation transients can be complex due to dynamically changing variables, such as spatial trap densities and electron concentration gradients, which are challenging to model and determine experimentally. Time-domain analysis of the transients, as explored in Paper I, can be used to qualitatively assigned to specific limiting processes.

Charge Extraction
The density of electrical charge stored in a solar cell device, whilst operating under steady-state operating conditions, can be estimated using charge extraction.54,55 Typically, charge extraction is obtained from illumination under short-circuit \( Q_{SC} \) and open-circuit \( Q_{OC} \) conditions, which is then used for qualitative comparisons between similar devices or a device subjected to various conditions. The acquisition sequence for determining \( Q_{SC} \) is illustrated in Figure 13c, which is calculated from the cumulative integral of the photocurrent decay transient.

This can be used to characterise the device under any operating condition and applied bias, along the J-V curve.

Open-Circuit Voltage Decay
The large perturbation open-circuit voltage decay transient can be obtained by measuring the voltage response directly after switching off the light source. This can be used as a relatively quick method for deriving the electron lifetime. The electron lifetime can be determined from the open-circuit voltage transient as follows56:

\[
\tau_n = - \frac{k_B T}{e} \int \frac{dV_{OC}}{dt}
\]

where \( \tau_n \) is the electron lifetime at a given potential, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( e \) is the elementary charge, \( dV_{OC}/dt \) represents the reciprocal derivative of the transient decay at a given potential.

Small Perturbation Transients
Assuming a number of approximations, the average electron recombination lifetime \( \tau_\rho \) and electron transport \( \tau_{Tr} \) time can be determined from small-perturbation transient techniques.55,57,58 Essentially, the subsequent phototransient decay following a small optical perturbation applied under various
steady-state operating conditions, is used to calculate a specific relaxation process. The former \( (\tau_g) \) can be calculated from small-perturbation photovoltage decay transients, obtained under steady-state open-circuit conditions. The latter \( (\tau_{tr}) \) can be determined from a single exponential fit to the photocurrent decay transient, following a small optical perturbation, under steady-state short circuit conditions.

The optical perturbation can be implemented through either a secondary light source (such as a laser or LED), or simply incorporated into the same background light source as a modulated pulse in intensity. The former may have has the advantage of allowing the excitation wavelength to be tuned. The latter is simply easier to implement.

**Electrochemical Impedance Spectroscopy**

At its core, electrochemical impedance spectroscopy (EIS) is an experimental method for characterising the dielectric properties of an electrical system. This technique is typically carried out under steady-state conditions, whereby the variable modulating frequency in potential is applied as small perturbation to the sample. EIS is a subset the lumped element model, which essentially assumes that complex electrical systems can reasonably approximated, as a combination of simpler idealised circuit elements – such as resistors, capacitors and inductors. This allows for the AC circuit to be inferred and modelled, in terms of an equivalent circuit. With a complete model, it is also possible to extend EIS to the mathematical modelling of device properties and even simulations of \( J-V \) curves and other experimental data.\(^{59}\) This makes EIS an especially powerful tool for providing comprehensive information about a system, provided that the device is not prone to drift and an accurate equivalent circuit model is available.

Under open-circuit illumination conditions, DSSCs typically exhibit three semi-circles in a Nyquist plot. From higher to lower frequencies, this corresponds to charge transfer resistance at the counter electrode, electron back recombination at the \( \text{TiO}_2/\text{dye/electrolyte} \) interface, and the diffusion resistance of the redox mediator.

Some useful parameters can be obtained from EIS. The diffusion resistance can be described by:

\[
R_{\text{diff}} = \frac{RTl}{z^2F^2AcD}
\]

where \( R \) is that gas constant, \( T \) is the absolute temperature, \( l \) is the diffusion path length, \( z \) is the number of charges carried by the redox species, \( F \) is the Faraday constant, \( A \) is the area, \( c \) is the concentration of the redox species, and \( D \) is the diffusion coefficient of the redox species.
However, EIS has certain limitations that make it unsuitable for characterising certain devices. Firstly, there must be a robust equivalent circuit model supported by substantial experimental data to allow for accurate fitting and interpretation of the data. Secondly, typical EIS measurements are carried out via single-sine acquisitions, that become asymptotically slower towards lower frequency ranges. Devices prone to drift, especially under prolonged light soaking, can significantly distort the data. For example, typical measurements apply a perturbation amplitude of \(~10\) mV, which ideally requires \(>1\) mV of drift by the device for the entirety of the measurement.

### Mass Diffusivity Equations

In DSSCs, the separation of charge carriers in liquid-junction DSSCs is primarily driven by diffusion, and not via a built-in electric field. Due to the typically strong ionic strength electrolytes, the effects of electromigration can largely be ignored. The mass transport of the redox mediators is primarily driven by concentration gradients. The effective diffusion coefficient \(D_e\) of the diffusion of species through porous medium can be described as follows:

\[
D_e = \frac{D \varepsilon_T \delta}{\tau}
\]

where \(D\) is the diffusion coefficient of the species in bulk electrolyte, \(\varepsilon_T\) is the porosity of the medium, \(\delta\) is the constrictivity and \(\tau\) is the tortuosity. Except for \(D\), the other coefficients are dimensionless variables which describe the porous medium. The porosity of TiO\(_2\) films prepared from DSL18NR-T paste typically have void porosities of 0.55. Constrictivity describes the resistance to transport through porous medium, which tends to increase in viscosity of fluid as the diameter of the diffusion species. When the diameter of the diffusing species approaches that of the pore volume, there may be increased electrostatic surface interactions between the cations and the TiO\(_2\) film, which would effectively slow down diffusion. Lastly, tortuosity describes the relative twists or tortuous path through the mesoporous medium.

Also, the issue of mass transport is expected to be exacerbated at lower temperatures and for higher viscosities, as defined by the Stokes-Einstein-Sutherland equation:

\[
D = \frac{k_B T}{6\pi \eta r}
\]

where \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(\eta\) is the dynamic viscosity and \(r\) is the radius of the spherical species.
Results and Discussion

The results of Papers I-VI have been categorised into focused discussions on specific aspects of mass transport limitation. This has further been divided into two key sections pertaining to the characterisation and the development of practical strategies for circumventing these issues. The overall goal has been to apply the cumulative findings from each of these works, to achieving higher performing devices based on more practical feasible viscous electrolytes.

Understanding The Implication of Mass Transport Limitations

Characterisation of Mass Transport Limitations

In Paper I, mass transport kinetics of the [Co(bipy)3]3+ oxidised redox mediator was investigated specifically with respect to the electrolyte-infiltrated medium. By exploiting inhomogeneous light absorption across the sensitised photoanode, and using time-domain transient analysis, mass transport limitations were indirectly observed via excess recombination.

Figure 16. Schematic depicting a cross-section of a DSSC, subjected to various illumination wavelengths, which have different depth penetrations into the film.
UV-Vis measurements showed that for LEG4-sensitised films, the light depth penetration ($\delta_p$) of 460 - 660 nm light ranged from 1.8 – 34.7 µm. As shown in Figure 16, this allowed for the photogeneration profile to be controlled with respect to illumination wavelength and direction; direction of illumination can either enter via the front-facing substrate electrode (SE)-side, or conversely, via the electrolyte-electrode (EE) side. Importantly, this affects the relative distribution of $[\text{Co(bipy)}_3]^{3+}$ spatially photogenerated throughout the film.

Figure 17. a-b) Steady-state short-circuit photocurrent ($J_{SS}$) compared versus light intensity. SE/EE-illumination (solid/open markers). c-f) Short-circuit photocurrent turn-on transients, following dark to 1 Sun illumination. SE-illumination (top) and EE-illumination (bottom). Photoanode thickness and illumination wavelength (blue, green, white and red illumination).

Most notably, Figure 17 showed that stronger EE-side absorption results in significantly higher photocurrent linearity and steady-state photocurrent output ($J_{SS}$). Conversely, strong SE-side absorption leads to lower $J_{SS}$, which related to mass transport limitations of $[\text{Co(bipy)}_3]^{3+}$ on the $10^{-2}$ - 1 s timescale. Also, biphasic turn-on rise transients were observed for EE-illumination, which was shown to relate to a delay ($t_{COL}$) in electron collection through TiO$_2$ film, and sufficient filling of traps at the FTO/TiO$_2$ interface. This was corroborated via direct linear correlation for $t_{COL}$ and the electron transport time-constant ($t_{tr}$) obtained from small perturbation transients. Also, this was consistent with previously reported trends for iodide based DSSCs.$^{60}$

The analysis of charge extraction decay transients in Figure 18 was used to qualitatively observe excess recombination, relative to the spatial photogeneration profile. For strongly SE-absorbing devices and higher light intensities, a reverse flow of current back into the device in the dark was observed. This showed that excess $[\text{Co(bipy)}_3]^{3+}$ accumulated at the FTO/TiO$_2$ interface, which caused a net flow of electrons from the external circuit to flow back into the device. Moreover, a secondary rise can be observed for thicker films,
due to a greater net accumulation of electrons trapped inside the TiO₂ film, unable to flow out due to charge conservation, until sufficient electron recombination or [Co(bipy)₃]³⁺ reaches the CE. Similar trends could also be observed for small perturbation transients, under steady-state illumination conditions. Overall, stronger SE-absorption contributed to non-linear recombination at higher intensities, leading to emergence of sub-linear deviations in $Q_{SC}$ and $\tau_{tr}$; whereas, these values were essentially invariant with respect to wavelength under EE-illumination. The latter indicates that EE-side illumination can be used to improve measurement accuracy, which is consistent with literature findings.⁶¹,⁶²

**Figure 18.** Normalised charge extraction decay transients obtained in dark, compared for effects of a-b) light intensity c-d) illumination wavelength.

**Figure 19.** Short-circuit photocurrent response following a square wave modulation in light intensity. SE- and EE- illumination direction compared. Baseline subtracted. A-B) the effect of increasing light intensity (0.1 – 2 Suns) and C-D) the effect of illumination wavelength.
MPP Stability testing

Accelerated stability testing under continuous 1 Sun illumination and active MPP-tracking was used for preliminary screening of any potential instability introduced into the new DSSC devices developed in Papers III & IV. However, it should be noted that water and acetonitrile based electrolytes remain relatively volatile and are not particularly well suited for long-term outdoor operation.

In Paper III, the MPP stability of aqueous cobalt electrolyte based DSSCs were investigated, as shown in Figure 20. Most notably, the devices exhibit significant gradual increase in photocurrent over the first day of light soaking. To exclude these effects from overestimating photostability, the nominal starting point for stability tracking was normalised with from the peak PCE value. The reason for the slow gradual rise in PCE was not entirely clear.

Also, periodic J-V scans were automatically conducted every 5 hours, which resulted in period spikes in MPP efficiency, especially noticeable after 100 h. This was even more evident in degraded cells. After applying forward bias potentials in each J-V measurements, a temporary enhance in photocurrent was observed. This may be attributed to a transient increase in Co²⁺ species photogenerated inside the mesoporous photoanode.

![Figure 20](image.png)

Figure 20. Evolution of PCE over 200 h 1 Sun continuous illumination under MPP and 25 °C. Three sets of cells compared: based on various redox mediators.
In **Paper IV**, the photostability of the TPAA additive was investigated. Following dye regeneration via TPAA, a positive radical cation is formed, which is in turn subsequently reduced by the Co$^{2+}$ species. The latter occurs within 3.5 µs. Thus accelerated MPP stability testing was used to access whether any significant degradation can occur via chemical side reactions via the TPAA radical. Most notably, **Figure 21**, shows negligible changes in the efficiency occurred after 250h testing. Small decreases in photocurrent can be attributed to electrolyte leakage. Over the 250h testing cycle, the devices outputted photocurrent densities of ~10 mAcm$^{-2}$ which corresponds to approximately 9000 C of charge passing through the device. For these devices, which had approximate dye coverage of 10$^{-7}$ molcm$^{-2}$, this corresponds to about 10$^6$ turnovers for the dye. Also, unlike the devices in **Paper III**, identical J-V and MPP efficiencies were obtained, with minimal hysteresis effects. Nevertheless, the statistical stability of devices was especially poor, with a large number of devices failing due to electrolyte leakage. Again, this reinforces the need to replace acetonitrile with a less volatile solvent, before any serious considerations for long-term stability can be investigated.

**Figure 21.** MPP stability of cobalt/TPAA/ACN DSSC. The evolution of normalised J-V parameters and MPP efficiency was characterised for 250 h continuous 1 Sun MPP tracking. J-Vs periodically scanned every 6 h. Nominal cell efficiency 9.7 % PCE.
The Impact of Temperature on Mass Transport

The effects of temperature on the resulting mass transport of 3-methoxypropionitrile cobalt based devices was investigated in Paper V. Temperature effects are especially relevant to the real-world operating conditions which may be subject to fluctuating temperature. Moreover, lower temperature can exacerbate mass transport limitations due to diminished diffusion.

Figure 22. Photocurrent Turn-on transients compared as a function of temperature (5 – 60 °C), versus SE/EE illumination directionality.

Figure 22 shows significantly lower photocurrent due to mass transport limitations, especially for SE-illuminated devices subjected to colder temperatures. Furthermore, this contributed to increased $J-V$ hysteresis and longer MPP stabilisation times, which exceeded 20 s. Conversely, EE-illuminated devices exhibited substantially less $J-V$ hysteresis and MPP rapidly stabilised in >1 s. The longer drift in stabilised photocurrent output directly relates to excess electron recombination to [Co(bipy)$_3$]$^{3+}$ at the FTO interface, as shown in Paper I. The addition of TPAA has negligible improvements to overall mass transport limitations, which remains solely limited based on Co$^{3+}$ diffusion to the CE.

Also, $J-V$ characterisation also showed that EE-illuminated devices exhibited superior $V_{OC}$, which was consistent with longer open-circuit voltage decay transients shown in Figure 23. These transients were used to derive electron lifetime, which was compared at 0.6 V as a function of temperature, to determine activation energies of 0.32 and 0.26 eV, for SE- and EE-illumination, respectively. Electron lifetimes were twice as long for EE-illuminated counterparts, which is consistent with reduced electron back recombination due to less [Co(bipy)$_3$]$^{3+}$ species being photogeneration closer to the TiO$_2$/FTO interface.
Additionally, EIS measurements showed ~40% lower diffusion resistance ($R_D$) for EE-illumination, which is consistent with reduced effective diffusion path length through the mesoporous TiO$_2$ medium. Activations energies of 0.18 eV were determined for diffusion. Moreover, the charge transfer resistance at the Pt counter electrode ($R_{CE}$) was found to be highly temperature activated process, with activation energies of 0.19 eV determined for both SE/EE-illumination directionality, respectively. Overall, this was consistent with the higher $FF$ and $V_{OC}$ observed for EE-illuminated devices.
Practical Solutions for Overcoming Mass Transport Limitations

Various practical strategies were developed throughout Papers II - VI in order to mitigate the mass transport limitations of the oxidised redox mediator.

Minimising the Bulk Electrolyte Diffusion Distance

In Paper II, the inter-electrode spacing was effectively eliminated by directly sandwiching together the complementary electrodes using an epoxy resin. This was achieved by directly electrodes clamping together, and applying epoxy around the exterior edges. Following an overnight curing period in air, the electrolyte was introduced through a pre-drilled hole via vacuum backfiltration. This procedure utilised a PEDOT/FTO counter electrode, which provided sufficient shunt resistance for some inter-electrode contact. In this work, three different DSSC sandwich architectures were compared, as shown in Figure 25.

Figure 25. Schematic illustration of DSSC sandwich structure and the reduction in the inter-electrode distance obtained using the epoxy sealing method.

Significantly improved photocurrent and FF were observed for epoxy-sealed devices, owing to the reduction in bulk electrolyte diffusion distance. Interestingly, it was found that the devices improved in PCE gradually after ~1 week of storage in the dark. The best device was obtained using epoxy-sealing with 8.2 % PCE. The addition of a ZrO2 layer topmost layer for the epoxy-sealed devices, also improved the reproducibility. This led to a 100 mV improvement in $V_{OC}$, which was equally offset by a loss in photocurrent, resulting in similar efficiencies. The latter could mainly be attributed to slight lower mass transport which was visible in terms of lower $J_{SS}$ in Figure 26, and higher $R_P$ in Figure 27. Dye-desorption measurements should that ZrO2 films had greater dye coverage than respective TiO2 films, which may have increased the effective constrictivity.
Figure 26. Photocurrent turn-on transient measurements comparing various DSSC-sandwich structures. A) normalised photocurrent transient. B) Photocurrent linearity.

Figure 27. Nyquist plots comparing Surlyn and epoxy sealed devices (top), and equivalent circuit with additional inductive element (below).

EIS showed that inductance could be observed for epoxy-sealed devices, at lower frequencies, owing to direct contact between the sensitised photoanode and PEDOT/FTO counter-electrode. The standard equivalent circuit was modified with an additional inductive element, shown in Figure 27.

Similarly, in Papers III, V & VI, the inter-electrode spacing was minimised albeit via greater compression of the thermoplastic spacers. Moreover, it was found that a small degree of contact between the dye-sensitised TiO₂ film and Pt counter electrode was possible, with negligible effects on J-V performance, provided that the shunt resistance exceeded ~20 MΩ.
Maximising Electrolyte-Infiltration for Aqueous Electrolyte DSSCs and Redox Mediator Solubility

In Paper III, an aqueous based electrolyte was used to replace acetonitrile, in conjunction with cobalt trisbipyridine redox mediators. A record PCE of 5.7% was achieved after addressing several key limitations. Firstly, the lack of redox mediator solubility is a severe issue for device performance. Table 2 shows the solubility of various cobalt polypyridine complexes in water. Due to the poor solubility of [Co(bipy)₃](NO₃)₂, continuous 60 °C heating was required to even dissolve the electrolyte, for device fabrication and for J-V characterisation measurements.⁶³,⁶⁴ However, it was found that dubious heating was not required, since greater solubility could be achieved by substituting the nitrate counterions with chloride. Transient absorption spectroscopy (TAS) measurements were conducted to obtain regeneration time constants of 1.5 and 3.5 µs, for aqueous and standard ACN electrolytes, respectively – which showed that 0.13 M was a sufficient concentration for regeneration.

Table 2. Solubility of cobalt polypyridine complexes in water (room temperature)

<table>
<thead>
<tr>
<th>Cobalt complex</th>
<th>Solubility / M</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="NO%E2%82%83">Co(bipy)₃</a>₂</td>
<td>0.09</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Co(bipy)₃</a>₃</td>
<td>&gt;0.2</td>
</tr>
<tr>
<td>[Co(bipy)₃]Cl₂</td>
<td>0.13</td>
</tr>
<tr>
<td>[Co(bipy)₃]Cl₃</td>
<td>&gt;0.2</td>
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<tr>
<td>[Co(phen)₃]Cl₂</td>
<td>0.09</td>
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<tr>
<td>[Co(phen)₃]Cl₃</td>
<td>&gt;0.2</td>
</tr>
<tr>
<td>[Co(bipy-pz)₃]Cl₂</td>
<td>&gt;0.2</td>
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<tr>
<td>[Co(bipy-pz)₃]Cl₃</td>
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Also, the hydrophobicity of the dye structure may limit the electrolyte infiltration of the photoanode due to insufficient wetting of the aqueous electrolyte.⁴⁶,⁴⁷ In order to facilitate better wetting, D51 was used instead of LEG4, as depicted in Figure 7. Most notably, D51 has shorter dimethoxyphenyl groups which can be expected to increase hydrophilicity, relative to the longer dibutoxyphenyl chains on LEG4. The improved wetting of D51-sensitised films, relative to LEG4, was confirmed by measuring the contact angle of pure water on the respective sensitised films. The D51-sensitised films showed complete wetting whereas the LEG4-sensitised films exhibited a ~105° contact angle. Conveniently, this eliminated the requirement for additional electrolytic surfactants and co-absorbers.
Suppressing Recombination at the Electrolyte/TiO₂ interface

Due to the faster electron back recombination kinetics of [Co(bipy)₃]³⁺ relative to iodide/triiodide, several important modifications are required, to reduce recombination at the electrolyte/TiO₂ interface. As shown in Figure 7, the dye-sensitisers used throughout Papers I-VI, with the exception of Paper III, require sterically bulky alkyl chains to suppress recombination at the electrolyte/TiO₂ interface.

In Paper IV, a small organic electron donor, tris(4-methoxyphenyl)amine (TPAA), was introduced into the standard cobalt electrolyte. A two-step electron transfer process was identified using transient absorption spectroscopy (TAS) measurements, where enhanced dye regeneration on the timescale of 100 ps – 10 ns was observed, and attributed to the formation of TPAA⁺ radical cation, which is subsequent regenerated by the [Co(bipy)₃]²⁺ species on the 14 µs timescale. Overall, TPAA facilitates an intermediary electron donor to the dye, which constitutes a two-step electron transfer process, as depicted in Figure 28. This resulted in a substantial improvement to both $J_{SC}$ and $V_{OC}$, leading to an improvement ~30% improvement in PCE, which is largely attributed to significantly reduced electron back recombination to the oxidised dye.

Figure 28. Charge transfer scheme of DSSC consisting of tandem cobalt trisbipyridine/TPAA electrolyte, and the approximate time constants for recombination (red) and regeneration (blue).
Figure 29. J-V graph comparing devices with and without TPAA, and LEG4 vs. D35:DB sensitisation.

In Paper VI, further suppression of electron-electrolyte back recombination via the sensitisation of co-absorber was investigated, which are shown in Figure 30. Chenodeoxycholic acid is a common co-absorber introduced to the sensitisation process, which has been shown to enhance both photocurrent and photovoltage, despite reducing overall dye-coverage.\(^65\)\(^{–}^67\) Further, the co-sensitisation of co-absorber with alkyl chains has been suggested to provide greater coverage of the TiO\(_2\) surface area suppressing electron-electrolyte recombination.\(^26\)\(^{,}^68\)\(^{,}^69\) The effect of chenodeoxycholic acid (Cheno) and alkyltrimethoxysilanes (AS) are discussed in more detail in the next section.

Figure 30. Chemical structure of chenodeoxycholic acid, alkyl functionalised trimethoxysilanes (where \(R = C_{18}H_{37}, C_{16}H_{33}, C_3H_7\) and \(C_8H_{17}\); which corresponds to octadecyltrimethoxysilane, hexadecyltrimethoxysilane, propyltrimethoxysilane and isooctyltrimethoxysilane, respectively.)
Optimising the Spatial Photogeneration Profile for Mass Transport

The aim of Paper VI was to maximise efficiency for devices with more viscous 3-methoxypropionitrile cobalt bipyridine electrolyte. The effective diffusion of redox species has greatly diminished when travelling through a dye-sensitised TiO2 medium, as opposed to a bulk electrolyte medium.70 This was corroborated in Papers I and V, and shown to be slightly improved by simply illuminated devices from EE-side. This principle is taken one step further in Paper VI, which attempts to directly engineering spatially variant porosity and dye coverage profile across the photoanode. The effects of increasing TiO2 porosity have been previously investigated in terms of increasing the amount of decomposable ethyl cellulose binder,71 reducing the concentration of TiCl4 treatment,72 or by using large sized TiO2 particles to introduce interstitial macropores.73 Similar principles were exploited in Paper VI via ethyl cellulose dilution and addition of 150-250 nm sized TiO2 scattering particles. Figure 31 shows the proposed optimal TiO2 structure for maximal mass transport. Scattering particles and ethyl cellulose are introduced into the bottommost layers, in order to increase spatially increase the porosity and minimise surface area for dye-absorption, towards the SE-side. The final topmost “capping” layer without intentionally left undiluted, in order to maximise photogeneration toward the EE-side. The presence of a capping layer is compared below. Devices without capping layers had a thicker diluted transparent TiO2 layer. Overall photoanode thicknesses was limited to 8 µm for comparison.

Figure 31. Artist depiction of spatially optimised TiO2 structure. Not to scale. Decreasing porosity towards uppermost layer. Mixed scattering (MS) layer, more porous transparent layer (TL) and less porous transparent capping layer (CAP).
Figure 32. J-V graph of EE-illuminated champion device from Paper VI, comparing the effects of TiO₂ capping layer. Lower concentration of scattering particles (15%) allowed for greater SE-side performance.

Most notably, Figure 32 showed that SE-illuminated cells performed with a capping layer and higher co-absorber concentration. Conversely, EE-illuminated devices perform better with higher current in the absence of a capping layer and with lower co-absorber concentration. The explanation for these effects were more apparent after turn-on transients and EIS analysis. A record PCE of 9.24 % was achieved, with current density of 16.6 mAcm⁻². This exceeds the photocurrent output of equivalent devices with ACN electrolytes from Paper IV, showing demonstrating that the feasibility of replacing MPN for replacing ACN electrolytes.

Figure 33. Short-circuit photocurrent turn-on transient compared for SE-illumination (left) and EE-illumination (right) for devices with and without TiO₂ capping layers. Effect of co-absorbers also compared.
The lower diffusion resistance ($R_D$) observed in Figure 27 for SE-illuminated devices with a capping layer, is consistent with the improved steady-state stabilised photocurrent ($J_{SS}$) observed in Figure 26. Furthermore, Figure 27 shows a consistent trend of decreasing $R_D$ as the co-absorber concentration increases, for both SE/EE-illuminated devices, which is consistent with improved mass transport through the mesopores. However, for uncapped devices with higher co-absorber concentration, Figure 33 also shows a trend of decreasing maxima peak current ($J_{Peak}$) with which may be indicative of reduced dye coverage limiting the maximum light absorption. For EE-illumination, the addition of a capping layer increases $t_{COL}$, which also exhibits lower rise slope as co-absorber concentration increases. This shows that longer time is required to sufficiently accumulate traps at the FTO/TiO$_2$ interface, which is consistent with reduced depth penetration of light reaching the SE-side. By converse analogy this is also consistent with the lower $t_{COL}$ observed for uncapped devices. The initial leftmost portion of the rise transient is steeper for devices with less co-absorbers, which is consistent with increased dye coverage leading to steeper electron concentration gradients.

Figure 34 also shows significantly lower $R_D$ for EE-illuminated counterparts, which is consistent with the higher FF observed in the J-Vs. Strangely, the presence of a capping layer consistently significantly improves $R_{CE}$ for both SE/EE-illumination directionality. The explanation for this is not entirely clear, however, may relate to differences in the spatial redox potential profile.
Conclusions and Outlook

In order for ongoing DSSC research to be taken seriously as a potential commercially viable product, the volatile acetonitrile electrolyte component must be eliminated. Thus far, this has been especially challenging for bulkier cobalt polypyridine complex redox mediators, which tend to have worse mass transport that becomes exacerbated for higher viscosity solvents and lower temperatures. The work in this thesis contributed to improved understanding and novel solutions for overcoming mass transport limitations.

The minimisation of the inter-electrode spacing was a critical for reducing the average diffusion distance through the bulk electrolyte, which could be either eliminated or substantially reduced, as shown in Papers II & III, respectively. Furthermore, Papers I, V & VI demonstrates that the average distance through the electrolyte-infiltrated mesoporous TiO$_2$ medium is a critical limiting factor for mass transport, which can be reduced by maximising the spatial photogeneration profile towards the electrolyte-electrode (EE) side. This also reduced electron-electrolyte recombination at the FTO/TiO$_2$ interface, leading to higher open-circuit potentials.

Further suppression of electron back recombination was achieved through the addition of an intermediary small electron donor (TPAA), used throughout Papers IV, V & VI, which greatly enhanced dye regeneration and increased electron lifetimes. Additionally, in Paper VI, chenodeoxycholic acid and alkyl trimethoxysilanes were used to further suppress recombination by providing better TiO$_2$ surface coverage, and facilitate improved mass transport.

Alternative less volatile electrolyte solvents were investigated to replace acetonitrile, throughout Papers III, V and VI. The challenges for aqueous based DSSC systems required optimisations of redox mediator solubility and hydrophilic dyes for sufficient electrolyte wetting, in order for sufficient electrolyte infiltration of the photoanode. The exacerbated issue of mass transport at lower temperatures was investigated in Papers V, and shown to exhibit superior performance under back-side illumination via the EE-side.

The culmination of all the aforementioned works were applied to Paper VI, to attain 9.2 % record PCE for cobalt 3-methoxypropionitrile electrolyte DSSCs, with superior current densities to previously published ACN-based systems. These promising results should encourage the replacement of acetonitrile and further optimisation development towards based on high viscosity electrolyte systems.
“Global warming”, also known as climate change, has been a hotly debated topic amongst scientists and politicians. Over the decades, there has been an overwhelming amount of evidence, gathered by international collaboration amongst scientists, which provides little doubt that mankind’s greenhouse gas emissions have induced drastic changes in the global climate. This continues to be a major challenge as global energy demands continue to grow, especially in developing nations. Some of the consequences of climate change can already being be observed, especially in certain parts of the world.

As global temperatures continue to increase, the desertification of more landmass is anticipated and prolonged periods of droughts are expected. This not only leads to the loss of habitable land, but can also lead to severe ecological disasters such as dust storms. Such post-apocalyptic imagery has been epitomised by the Dust Bowl of the 1930s, where severe topsoil erosion coupled with wind led to literal black blizzards, darkening skies and buried landscapes, which travelled across the US continent.

*Figure 35.* Dust bowl of the 1930s which struck U.S. and Canadian prairies. Source: United States Department of Agriculture.
Globally increased CO₂ levels can also lead to ocean acidification due to increasing amounts of CO₂ dissolving in water, forming carbonic acid. This severely disrupts oceanic life, and some of its harmful effects have already been widely observed. The increasing concentration of carbonate ions disrupts the calcination process required for building the shells and skeletons of many oceanic lifeforms. Increased ocean acidity can induce harmful metabolic responses in some oceanic species. Where once there were plentiful vibrant corals reefs, the increased acidity has led to widespread coral bleaching, painting an underwater desert landscape. Also, in the long-term, the loss of coastal land regions due to flooding is anticipated, due to rising sea levels largely contributed to melting ice sheets and glaciers in Greenland and Antarctica. All of the above factors can lead to other effects such as extinction risks, forced migrations and food insecurity.

The impending consequences of climate change have been a major motivation for the research into “renewable” energy production, which generate electricity by releasing less CO₂ or other greenhouse gases. This can be achieved by directly tapping into naturally replenishable energy resources such as solar, wind, hydro, geothermal energy and biofuels.

Photovoltaic devices such as dye-sensitised solar cells (DSSCs) harness energy from light to produce electricity. DSSCs have certain advantages over other PV technologies such as higher performance under low-light conditions, and colour tuneable semi-transparent appearance, which may possibly enable niche applications of DSSCs for building-integrated or indoor applications. Unfortunately, the best performing DSSCs tend to break down very fast due to leakage of its liquid electrolyte. Even worse, when this is replaced with a more stable electrolyte, the performance tends to drop drastically due to increased viscosity of electrolyte, which limits the ability of ions to move through the electrolyte. In order to generate electric current, the ions in the electrolyte need to travel to the counter electrode in order to complete the electric circuit. The work in this thesis contributes to developing strategies for reducing the ion travelling distance, which allows for higher performance with more stable viscous electrolytes. This was achieved in two ways – firstly, by minimising the overall thickness of the electrolyte layer, by compressing the electrode separation distance to a maximum. Second, the light absorption across the material was deliberately made more disproportional, such that a greater portion of light was absorbed relatively closer to the counter electrode, which subsequently also reduced the average distance that the ions need to travel through the light absorbing material. Overall, further development of DSSCs with more practical stable electrolytes is absolutely necessary, in order for it to be seriously considered as a contender in the competitive PV industry.
"Global uppvärmning", även känd som klimatförändring, har varit ett diskutabelt ämne bland forskare och politiker. Under årtiondena har det skett en överväldigande mängd bevis som samlats in av internationell samverkan bland forskare, vilket ger lite tvivel om att mänsklighetens växthusgasutsläpp har orsakat drastiska förändringar i det globala klimatet. Detta fortsätter att vara en stor utmaning då globala energibehov fortsätter att växa, särskilt i utvecklingsländerna. Några av konsekvenserna av klimatförändringen kan redan observeras, särskilt i vissa delar av världen.

Eftersom de globala temperaturerna fortsätter att öka, förväntas ökenspridningen av mer markmassa och långa perioder av torka förväntas. Detta leder inte bara till förlusten av beboelig mark, men kan också leda till allvarliga ekologiska katastrofer som dammstormar. Sådana post-apokalyptiska bilder har blivit epitomiserad av Dammkålen från 1930-talet, där allvarlig övrig erosion kopplad till vind ledde till bokstavliga svarta snöstormar, mörkare himmel och begravda landskap som reste över den amerikanska kontinenten.

Figure 36. Dammkål från 1930-talet som drabbade amerikanska och kanadensiska prärier. Källa: Förenta staternas Department of Agriculture.

De förestående konsekvenserna av klimatförändringen har varit en viktig motivering för forskningen kring "förnybar" energiproduktion, som genererar el genom att släppa ut mindre koldioxid eller andra växthusgaser. Detta kan uppnås genom att direkt knacka på naturligt förnybara energiresurser som sol, vind, vattenkraft, geotermisk energi och biobränslen.

Fotovoltaiska enheter som färgkänsliga solceller (DSSCs) utnyttjar energi från ljus till elproduktion. DSSC har vissa fördelar jämfört med andra PV-teknologier, såsom högre prestanda under svagt ljus och färgtillförsel semitransparent utseende, vilket möjliggör nischanvändningar av DSSC för byggintegrierade eller inbyggda applikationer. Tyvärr tenderar de bäst fungerande DSSC att bryta ner mycket snabbt på grund av läckage av sin flytande elektrolyt. Ännu värre, när detta ersätts med en mer stabil elektrolyt tenderar prestandan att minska drastiskt på grund av ökad viscositet av elektrolyt, vilket begränsar jonernas förmåga att röra sig genom elektrolyten. För att generera elektrisk ström måste ionerna i elektrolyten resa till diskelektroden för att slutföra den elektriska kretsen. Arbetet i denna avhandling bidrar till att utveckla strategier för att minska jonresistansavståndet, vilket möjliggör högre prestanda med stabilare viskösa elektrolyter. Detta uppnådes på två sätt - för det första genom minimering av den totala tjockleken hos elektrolytiskt klyfta materiella med mer praktiska stabila elektrolyter absolut nödvändig för att den seriöst ska betraktas som en utmanare i den konkurrerande PV-industrin.
科普總結(中文)

"全球變暖"，也被稱為氣候變化，一直是科學家和政治家之間激烈爭論的話題。幾十年來，科學家之間的國際合作收集了大量證據，人類的溫室氣體排放毫無疑問已引起全球氣候的急劇變化。隨著全球能源需求持續增長，特別是在發展中國家，氣候變化將是一項持續性的重大挑戰。特別是在世界某些地區，可以觀察到氣候變化的一些後果。

隨著全球氣溫持續上升，預計將有更多陸地荒漠化和會出現長時間的干旱。這不僅會導致可居住的土地流失，還會導致嚴重的生態災難，如沙塵暴。這種後世界末日的圖像已經被 20 世紀 30 年代的沙塵暴所體現，其中嚴重的表土侵蝕與風一起導致了黑色暴風雪，天空的黑暗和景觀的掩埋，災難的景象貫穿了美國大陸。

因为二氧化碳溶解在水中的含量增加而形成碳酸，全球增加的二氧化碳水平也會導致海洋酸化。這嚴重擾亂了海洋生物，其中一些有害影響已被廣泛觀察到。碳酸根離子濃度的增加破壞了構建許多海洋生命形態的殼和骨架所需的煅燒過程，並且會在某些海洋物種中引起有害

![圖 34. 20 世紀 30 年代的沙塵暴侵襲了美國和加拿大的大草原。資料來源：美國農業部。](image-url)
的代謝反應。曾經有丰富多彩的珊瑚礁，酸度增加導致珊瑚氾濫，水下出現荒漠之觀。此外，從長遠來看，由於海平面上升導致綠地和南極洲的冰蓋和冰川融化，預計洪水會導致沿海陸地區域的流失。所有上述因素都可能導致其他的問題，如滅絕風險，強迫遷移和糧食不安全。

氣候變化即將發生的後果一直是研究“可再生”能源的一個主要動力，這種能源通過釋放更少的二氧化碳或其他溫室氣體來發電。這可以通過直接利用天然可補充的能源資源來實現，例如太陽能，風能，水能，地熱能和生物燃料。

諸如染料敏化太陽能電池（DSSC）的光伏器件利用來自光的能量來產生電力。DSSC 與其他光伏技術相比具有一定的優勢，例如在低光條件下具有更高的性能，以及可調色的半透明外觀，這可能使得 DSSC 適用於建築一體化或室內應用。不幸的是，性能最好的 DSSC 由於其液體電解質的洩漏而傾向於非常快地分解。更糟糕的是，當用更穩定的電解質代替時，由於電解質的粘度增加，性能趨於急劇下降，這限制了離子移動和通過電解質的能力。為了產生電流，電解質中的離子需要轉移到對電極以完成電路。本論文致力於研究減少離子移動距離，從而獲得更高性能和更穩定的粘性電解質。主要通過兩種方式加以實現：首先，通過將電極分離距離壓縮到最大值，使電解質層的總厚度最小化。其次，使更大部分材料上的光吸收更靠近對電極，使得離子需要穿過吸光材料平均距離減小。總體而言，為使 DSSC 成為競爭激烈的光伏產業中的競爭者，進一步開發具有更實用的穩定的電解質器件是非常有必要的。
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