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*Published in:*
FLEXIBLE AND PRINTED ELECTRONICS

*DOI:*
10.1088/2058-8585/aaabc9

Published: 30/03/2018

*Document Version*
Peer reviewed version

*Please cite the original version:*
Application of dye-sensitized and perovskite solar cells on flexible substrates

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Keywords: flexible solar cells, substrates, dye solar cells, perovskite solar cells

Abstract
In this paper, a review of applying dye-sensitized (DSC) and perovskite solar cells (PSC) on flexible substrates is presented. Metallic and polymeric materials are the most common flexible substrates used. Cell integration into a textile substrate is also considered here as a future alternative. Common challenges with these include penetration of humidity, cell stability, and lifetime. Flexible DSC and PSC solar cells are still a niche technology, but have an inherent potential for cheap roll-to-roll mass-production of photovoltaics.

1. Introduction
Photovoltaics (PV) is one of the fastest growing fields in energy technology. The average annual growth rate of PV has been close to 40% over the past ten years, with business value around $100 billion per annum [MIT 2015, Harry 2017, REN21 2017]. But the future prospects for PV look even better, e.g. in some scenarios PV stands even up to 50% of all electricity by 2050 [Haegel et al 2017]. More than 90% of the present PV market is based on silicon solar cells (monocrystalline or polycrystalline Si) and the rest is thin film solar cells. PV on flexible substrates mainly based on thin-films or nanostructures, constitute a minute share (<<1%) of the annual production of PV, which was 60,000 MWp in 2016 [REN21 2017]. Flexible solar cells are still mainly used in niche and special applications with less energy relevance..

At the same time, the cost of PV has dramatically dropped, or, by almost 90% in the last ten years [REN21 2017]. This is explained by the scale of economics, improved manufacturing processes, but also by the cost decrease of the key material components of the solar panel. The cost reduction in
photoactive, catalytic, or conductive materials used in the solar cell means that the relative importance of other materials such as the encapsulant and substrate will be more important in the future, which now constitute around 15-20% of the material cost of a silicon PV module [Horowitz et al 2017].

The future importance of flexible substrates is demonstrated by several other factors. As the scale of the main energy applications is large, substrate materials and cell structures lending for roll-to-roll mass production of PV are of interest, which in turn would favour flexible substrates such as plastics and metals over the traditional rigid glass substrates. In 3rd generation solar cells such as dye solar cells or organic solar cells, which utilize thin nanostructures, the amount of photoactive material needed is small (< 1 g per Wp) compared to the substrate (10-70 g/Wp), which puts more focus on the substrate to reduce the total weight of PV. The same applies for 2nd generation PV such as Amorphous Silicon (a-Si), Cadmium-Telluride (CdTe) or Copper Indium Gallium Diselenide (CIGS) technologies [Green 2007].

Envisioning PV as a mainstream energy technology would also require considering the availability of different substrate materials - typically a rigid substrate configuration would need much thicker layers and hence more material that a thin flexible substrate. For example, comparing the volume of global material production shows that when scaled to the gravimetric material demand of a PV substrate, global plastics or steel production could yield one to two orders of magnitude higher PV production volumes than glass. Flexibility also adds to functionality, which may be important for different applications in which form and shape are important and cannot be achieved with traditional planar structures. Importantly, all major PV technologies lend themselves to be used as flexible cells, including silicon solar cells.

Flexible substrates for traditional PV have received much attention in the past and are well covered by the scientific literature [Green 2007, Pagliaro et al 2008, Wang et al 2017]. The applicability of flexible substrates have been well demonstrated for thin-film and silicon photovoltaics technologies, which are based on physical deposition principles and semiconductor technology. In organic photovoltaics (OPV), flexible substrates are of central importance for the whole device concept and have therefore been extensively investigated and reported in the scientific literature [see e.g. Calagan et al 2011, Kaltenbrunner et al 2011, Lipomi and Bao 2011, Cao et al 2012Yun et al 2013, Kang et al 2014].

However, for future solar cell technologies such as dye solar cells (DSC) and perovskite solar cells (PSC), the substrate development is not yet that advanced, though it would be important to realize the full potential of these new cell types. Issues of importance for flexible substrates in this context include device stability, life-time, efficiency, among others, which have not yet been fully solved. The focus of
this paper is on applying these new solar cells types on flexible substrates, where the scientific literature is still scarcer than with thin-film solar cells, organic photovoltaics, or silicon solar cells. We don’t cover organic solar cells as these have already been extensively covered in the scientific literature [Krebs, 2009, Li et al 2017, Lu et al 2017] The focus of the paper is on introducing DSC and PSC for flexible substrates, which is highly relevant as the most common substrate for these solar cells is still glass. As this is a rather new subject, the aim is to present technologies and applications, with some special issues included. Therefore, considering more specifically the properties of the substrate such as transparency, thickness, barrier properties, possible improvements, etc. were outside the scope of this review, but could deserve an own review. Viewing the properties of the substrates per se would also have an important link to printed electronics e.g. on plastics, where ample of experience would be available.

This paper provides a review on flexible substrates for dye solar cells (DSC) and perovskite solar cells (PSC), and on some central issues linked to these. We start in Section 2 with a brief overview of flexible substrates for PV. In Sections 3 and 4, flexible substrates for DSC and PSC are presented including new manufacturing approaches for these. Section 5 presents an innovative case of DSC with flexible substrates, in which textiles form both a substrate for and an integral part of DSCs, This could provide new use of flexible DSCs as a kind of energy harvesting device. In Section 6 we discuss the challenges with cell life-time linked to the substrate, which is one of the main challenges with DSC and PSC. Finally, in Section 7 a summary is presented.

2. Brief insight into flexible PV substrates

Commercial products of flexible PV have been manufactured since the late 1980s, e.g. the US Energy Conversion Devices Ltd. (later Uni-Solar Ltd) manufactured with roll-to-roll processes a-Si solar cells on steel laminates well applicable for building-integrated applications. Figure 1 shows a triple-junction a-Si module from the 1990s with efficiency above 10%. The present state-of-the-art of thin-film flexible PV is well demonstrated in Figure 2, with a modern CIGS cell on stainless steel reaching a close to 15% efficiency [CIGS 2017], for which several manufactures can be found. Also, basic silicon solar cells, when sliced down to ~30μm demonstrate excellent mechanical flexibility [Ching-Chang Lin 2015, Yoon 2008, Blakers and Armour 2009]. However, the efficiency of flexible thin c-Si PV modules, would be well below glass modules, or 13-15% versus 20-22% for ordinary crystalline silicon cells [Fan et al 2008, Yoon et al 2008]. Organic photovoltaic modules employ thin plastic foils (e.g. PET, PEN) [Calagan et al 2011, Kang et
al 2014], typically below 0.2 mm, but even down to 2 μm [Kaltenbrunner et al 2011], or even rubber-like materials (e.g. PDMS) [Lipomi and Bao, 2011], which provide high flexibility. The up-scaling of OPVs and flexible substrates has also received attention [Carlé et al 2014].

Typical substrate materials used for PV include among others glass sheets, polymer films (Kapton®, Polyimide), PDMS, and metal foils [Padinger et al 2003, Fan and Javey 2008, Fan et al 2009, Znajdek et al 2016, Dupont 2017]. Flexible substrates for PV are also subject to different requirements such as [Pagilaro et al 2008]:

- high electrical insulating properties;
- transparency;
- flexibility;
- toughness;
- smoothness;
- functionalities;
- stability.

Challenges encountered with flexible substrates include humidity and corrosion. For perovskite and dye solar cells in particular, transparent flexible substrates, which efficiently block moisture penetration, would be highly relevant. Water is a major cause of degradation in many PV technologies and e.g. currently used PET/PEN substrates allow high moisture penetration.

Figure 1. A flexible triple-junction a-Si PV module (32Wp) from the 1990s.
3. Flexible substrates for dye-sensitized solar cells

Dye-sensitized solar cells (DSCs) amongst other emerging PV technologies have also been realized as a potential source of cheap electricity production (Low et al 2018, Wu et al 2017 Kalowekamo et al 2009, Hashmi et al 2011). Their unique features include low cost and plentiful availability of their active materials such as TiO$_2$, ZnO, carbon black, and graphite based nanoparticles as well as the possibility to deposit these materials by using cost-efficient and scalable methods such as screen printing or inkjet printing (Hashmi et al 2016, Hashmi et al 2015). The working principles of DSCs were initially demonstrated in early 90's by fabricating the devices on transparent conducting oxide (TCO) coated glass substrates (O’Regan et al 1991).

The use of non-permeable and transparent conducting glass provide great freedom to select high temperature processing in DSCs from the design to the deposition of their active materials (Hashmi et al 2011, Halme et al 2010). In this regard, efforts were made to develop screen printable pastes of some of the aforementioned active materials for both the photoelectrodes (PEs) and counter electrodes (CEs) of these traditional glass based DSCs (Ito et al 2007, Murakami et al 2006). These pastes normally utilize organic binders such as ethyl cellulose and high boiling based solvents e.g. terpineol to adjust the viscosity and compatibility of these active materials with the deposition method such as screen-printing. These screen printable pastes of the active materials, after their deposition, require a high temperature (400-550 °C) sintering step to remove the viscosity enhancing binders and solvents for the efficient charge transfer within the deposited layers at both the PEs and CEs (Ito et al 2007, Murakami et al
2006). This high temperature sintering step does not only improve the adhesion of the deposited layers with the glass substrates, but also provides a necking effect to promote the inter-particle connectivity between the individual nano-particles, which consequently improves the overall performance of the individual photovoltaic parameters of a DSC. These high temperature processes have always been used to demonstrate very high efficiencies for glass-based DSCs architecture, which provides a possibility for building integrated and aesthetic photovoltaics applications (Mathew et al 2013, Yella et al, 2012, Zhang et al 2014).

Despite providing plentiful advantages in terms of high conductivity and transparency as well as high efficiency and high stability, the heavy weight, rigidity, and fragility of these glass substrates restrict their use in many practical applications and rule out the possibility to use fast roll to roll (R2R) industrial manufacturing methods (Fakhruddin et al 2014).

Since the same printing methods (like screen printing, blade coating or inkjet printing) can also be utilized to produce DSCs on any desirable substrates, efforts have been made to transfer the working principle of DSCs on flexible substrates in numerous configurations as shown in Figure 3 to investigate their mass production with R2R production (Yamaguchi et al 2007, Park et al 2008, Hashmi et al 2011). In the following are details regarding the variety of flexible substrates, which have been used for flexible DSCs.

The flexible substrates based DSCs can be produced with numerous configurations as shown in Figure 3. However, every configuration has different pros and cons. For example, the use of transparent conducting oxide (TCO) coated polymers, such as tin-doped indium oxide on polyethyleneterephtalate (ITO-PET) and tin-doped indium oxide on polyethylenenaphthalate (ITO-PEN), allows minimum optical losses in the cell (Figure 1-a). The thickness of the PET would typically be 0.1-0.2 mm. However fabricating robust polymer based photoelectrode has been a critical issue for high performance polymer based flexible DSCs. One well-known reason is the temperature restriction (~ 150-170 °C), which is the critical limit of the deformation of these ITO-PET and ITO-PEN sheets and rules out the idea of using same high performance titania paste as used for glass based DSCs, which requires a high-temperature sintering step (450-550 °C) as described in the previous section. Hence, the low temperature TiO₂ nano-particles based layers exhibit poor mechanical adhesion and easily flake off from these substrates (Weerasinghe et al 2013, Hashmi et al 2011). Dye solar cells with plastic based photoelectrode substrates have been demonstrated with iodine-based electrolytes (Ikegami et al 2009, Zardetto et al 2013, Han et al 2015, Drygala et al 2017), which are less sensitive towards current leakage from
photoelectrode to the electrolyte compared to e.g. cobalt complex electrolytes. The use of such alternative electrolytes is further hindered by the fact that the low temperature manufacturing also limits the kind of blocking layers that can be employed (Miettunen et al 2009) as the construction of a blocking layer also requires heat-treatment. Even though blocking layers could be made at low temperature, their characteristics may significantly differ from layers made at high temperature; for example, an atomic layer deposited TiO$_2$ layer is amorphous at low temperature, but crystalline a high temperature with significantly higher conductivity (Miettunen et al 2009).

Figure 3. Different configurations of flexible DSCs. a) Traditional front illuminated DSC, b) Metal PE based reverse illuminated DSC, c) Front illuminated DSC with Plastic PE and Metal CE, d) Front illuminated DSC with Plastic PE and TCO free plastic CE, e) Flexible back contact DSC on metal substrate (PE = photo electrode, CE = counter electrode, TCO = Transparent conducting oxide such as tin-doped indium oxide or ITO Layer).
On the other hand, the use of thin 0.03-0.05 mm (Miettunen et al 2010) and highly flexible opaque metallic substrates overcomes the problem of using a high temperature sintering step as used for glass based PEs. However, in this configuration the reverse illumination as well as the stability of the devices is the key hurdle for reliable operation, in particular corrosion. Due to the reverse illumination (Figure 3b), the incident light on the semi-transparent CE gets absorption first by the catalyst material (e.g. semi-transparent Pt nano-particles based catalyst) and then by the semi-transparent electrolyte layer, which exchange ions during the cell operation. Additionally except for noble metals, the iodine-based electrolyte rapidly corrodes the low cost metals such as stainless steel (Miettunen et al 2013b, Miettunen et al 2015). Cobalt complex electrolyte is less prone towards corrosion and they allow using less noble metals such as stainless and ferritic steels (Miettunen et al 2013b, Miettunen et al 2014), which are cheaper compared to conducting glass substrates (Hashmi et al 2011). The corrosion issues are discussed in more detail in Section 6.

Moreover, the use of plastic substrates based PEs with metal based CEs (Figure 3c) may potentially reduce the resistive losses due to highly conductive CE. However, it combines the limitations as mentioned above both for the plastic based photo-electrodes and an expected corrosion with metals due to corrosive electrolytes. Therefore, plastic based PEs are typically combined with plastic based CEs. In such case, the CE can be realized as TCO free employing either opaque or semi-transparent polymer electrodes comprised of conductive non-metallic carbon nanotubes (CNT's) serving both as a TCO free conductive layer and as a catalyst for CEs (Hashmi et al 2013, Hashmi et al 2014, Hashmi et al 2014, Aitola et al 2012).

It is also possible to prepare a back contact cell configuration, i.e. where all layers are deposited on one substrate (Figure 3-e). In this configuration there is no conductive layer shadowing the active parts of the PE and it can be realized TCO free. Flexible back contact configurations have been demonstrated on metal substrate as well as on plastics (Fu et al 2013, Yoo et al 2015). Depositing the back contact cell on metal allows also preparation of all layers at high temperatures.

4. Flexible substrates for perovskite solar cells

Perovskite semiconductors based solar cells (PSCs) have recently received much attention worldwide due to their promising features, i.e. the strong panchromatic absorption of the sunlight and longer diffusion lengths of the charge carriers in perovskite semiconductors along with facile and identical
fabrication methods as opted for dye-sensitized solar cells (DSCs) and organic solar cells (OSCs) (Brushka et al 2013, Stranks et al 2013). The high performance of these PSCs (efficiency > 22%) has been demonstrated on FTO-Glass substrates (Yang et al 2017). However, alternative methods have also been developed to produce this potentially low cost photovoltaic technology on flexible substrates (Reddy et al 2017, Bi et al 2017, Giacomo et al 2016). In this regard, the same transparent conducting polymers ITO-PET and ITO-PEN substrates remained the most preferable choice in fabricating the PSCs on flexible substrates (Zardetto et al 2017, Zhou et al 2017, Giacomo et al 2016). Figure 4 represents the variety of configurations, which have been reported for PSCs with flexible substrates (Kumar et al 2013, Docampo et al 2013, Yoon et al 2017, Troughton et al 2015).

Since PSCs are solid state devices, the issues related to the chemical stability of their associate materials is somewhat different than the liquid electrolyte based DSCs, where the volatile electrolytes are not only responsible for the degradation in performance due to the leakage upon exposing them to stressful conditions, but were also found corrosive when integrated with metals based substrates (Miettunen et al 2013). Nevertheless, the issues related to the mechanical stability of the flexible PSCs are quite identical to flexible DSCs (Heo et al 2016). Moreover, the translation from rigid FTO-Glass substrates to flexible conducting polymers again restrict any high temperature processing of the fabricated materials for PSCs due to the deformation of flexible substrates (Giacomo et al 2016).

Interestingly, the planar structure of PSCs also allows great freedom to avoid the usage of the mesoporous electron and hole transporting layers (such as TiO₂ or carbon nanoparticles), which have not been found mechanically strong when fabricated for flexible DSCs via binder free pastes (Weerasinghe et al 2013, Miettunen et al 2013). In fact, the highest efficiency (> 15%) among any kind of flexible structures based PSC devices reported in the literature is achieved with planar structure based PSCs (Heo et al 2016).

The first demonstration of a flexible PSC was reported with the traditional n-i-p configuration (Figure 4a) on ITO-PET (sheet resistance, \(R_{Sh} = 60 \, \Omega/Sq\)) substrate, where the low temperature based electron selective compact and mesoporous layers of ZnO and ZnO nanorods were fabricated through electrodeposition and chemical bath deposition (CBD) methods respectively (Kumar et al 2013). This low temperature fabrication scheme for electron selective layers provided an opportunity to fabricate the whole stack on flexible conducting polymer substrate (i.e. ITO-PET) due to the inherent low temperature deposition methods and materials available for perovskite precursor, holes transporting material (HTM) i.e. Spiro-OMeTAD and metal electrodes deposition. Although the reported efficiencies were very low
(2.62%), this proof of concept greatly motivated other labs to further develop the low temperature materials and their processes to produce more efficient flexible PSCs.

As a result, >10% PSCs were validated for the very first time, again in n-i-p configuration with a low temperature ZnO electron transporting layer fabricated over ITO-PET polymer substrates. The other striking feature of this work was the mechanical bending test performed over fabricated flexible PSCs which also showed outstanding performance of these F-PSCs by retaining 85% of their initially measured conversion efficiencies when bended over 10 mm radius and suggested that highly robust PSCs may also be produced over flexible polymer substrates without compromising their photovoltaic performance (Liu et al 2014). This robust performance of the stack can be mainly concluded from the fact that planar PSCs contains very thin device structure (100-150 nm) in which the particle based films do not severely damage and maintain their performance when experiencing high mechanical stresses.

The conversion efficiency of the planar structure with conducting polymer substrates (e.g. ITO-PET and ITO-PEN) have continuously increased and the highest efficiency (15.6%) to date have been reported for the ITO-PEN substrates using a compact ZnO electron transport layer (Heo et al 2016). Additionally, the robustness of these flexible perovskite solar cells was also investigated with a cyclic bending test, which revealed good device performance stability when bended over a radius of 12 mm, whereas for the extreme limits, the efficiency was severely decreased (more than 50%) when bended over much smaller (4 mm) radius (Heo et al 2016).
On the other hand, the flexible perovskite solar cells have also been developed with a p-i-n configuration also known as inverted configuration (Figure 4b), which is actually inspired by the organic solar cells structure where the p-type holes transporting materials (HTM) can be deposited first over ITO layer of the transparent polymer substrate. After that, the perovskite light absorbing layer and electron transport layer (ETL) can then be deposited over this HTM to complete the structure (Figure 4b).

The PSCs with this configuration was first demonstrated by Docampo et al (2013) by utilizing the established organic solar cell materials, which were incorporated with perovskite layer on ITO-PET substrate. A conversion efficiency of 6.4% was achieved by integrating PEDOT:PSS and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) via spin coating as HTMs and ETL layers in the device structure, respectively. Furthermore, due to already available setup for organic solar cell fabrication in several labs worldwide, this configuration is also developed very rapidly, where several HTMs and ETLs have been integrated in the lab-sized PSCs devices and have shown a device efficiency up to 14.5% (Docampo et al 2013). However, the mechanical stability was not tested for these high efficiency inverted PSCs, which raise the question of the device performance stability at extreme bending (Heo et al 2016).

Similarly, the advancements in highly conductive single walled carbon nanotubes (SWCNTs, sheet resistance ranges from 250 Ω/Sq-50 Ω/Sq, Jeon et al 2017) or silver nano-wires (sheet resistance ~ 18-20 Ω/Sq) also offer a possibility to realize ITO free device structures of PSCs either on the same PET polymer to be used as bottom electrode (Jeon et al 2017) or to be used as a top electrode (Lee et al 2015) in case of using metal as a bottom electrode along with high transparency (Jeon et al 2017, Cui et al 2017, Lee et al 2016).

In addition to high transparency and high conductivity, these SWCNTs and silver nanowires (Jeon et al 2017, Cui et al 2017, Lee et al 2016) also provide excellent flexibility and may potentially exhibit robust bending features in large area flexible modules which has been considered a limitation for ITO layers (Heo et al 2016, Giacomo et al 2016). More promisingly, these aforementioned SWCNT and silver nanowires can also be omitted with only PEDOT:PSS, which does not serve only as HTM but at the same time can also be used as an efficient conductor in the device structure (Kaltenbrunner et al 2015). Hence combined with aforementioned good electrical conductivity, high transparency, and versatile choices for these materials to be used both as conductors and HTM’s at the same time, the concept of TCO free lab-sized flexible PSCs has also been developed as a sub-class of inverted PSCs (Jeon et al 2017, Li et al 2016) and has revealed efficiencies ranging from 5-14% (Dianetti et al 2015, Li et al 2016). As expressed above, this configuration has also demonstrated good stability and showed no performance degradation after
exposing to 25 cycles in a 25% cyclic compression and retained 70% of the initial efficiency after 100 cycles (Li et al 2016). More importantly these ultrathin (~3µm) flexible devices have also successfully been deployed for aviation applications thus endorsing their potential for other futuristic applications such as smart buildings or smart detectors and sensors (Li et al 2016).

Similar to dye-sensitized solar cells (DSCs), the perovskite configurations have also been produced on flexible metal foils (Nejand et al 2017, Lee et al 2016, Troughton et al 2015). The usage of opaque metal foils offer very high conductivity, possibility of employing high temperature processes to deploy electron transporting layer as well as non-permeability to oxygen and water. Nevertheless, the biggest limitation of metal foils is to realize again an inverted structure, where a highly transparent electrode is required to work as hole transporting layer along with an additional transparent polymer electrode for lamination, which could also provide resistance to the possible intrusion of moisture and humidity (Figure 4d).

In this regard, the first demonstration of this configuration was reported by Troughton et al, where the compact TiO$_2$, Al$_2$O$_3$, perovskite and Spiro OMeTAD layers were deposited via spin coating as electron transporting, insulating scaffold, light absorbing and holes transporting layers, respectively, followed by spray coating of the PEDOT:PSS layer. After that, a flexible electrode laminate consists of a mixture of PEDOT:PSS and pressure sensitive adhesive onto a PET foil embedded with a Ni grid. This electrode was bonded with the metal foil containing the complete structure. A device efficiency of 10.3% was achieved with very good mechanical stability (only 7% of the initial efficiency was lost) when subjected to a bending radius of 5 cm for 200 bending cycles.

To date the highest efficiency (13%) for these flexible metal foil based PSCs is reported with the same Titanium metal foil, which was incorporated with Titanium nanowires and TiO$_2$ nanoparticles to function as electron transporting layer which provided the rapid collection and transmission of photo-generated electrons (Xiao et al 2016). A separate ITO-PEN foil was coated with PEDOT:PSS and was bonded with clips whereas the perovskite precursor ink was introduced between the gaps of the two individual substrates. Although the device architecture exhibited high efficiency, it can, however, be consider only a proof of concept study since no procedure of device sealing and no stability data for long-term operation of the fabricated devices is provided.
Table 1 summarizes the best-reported efficiencies for each type of the aforementioned flexible PSCs along with details of electron and holes transporting layers, perovskite precursor and their deposition methods.

Table 1. Best reported efficiencies for each type of perovskite solar cells.

<table>
<thead>
<tr>
<th>Type of flexible substrate</th>
<th>Configuration</th>
<th>ETL and its deposition method</th>
<th>Perovskite deposition</th>
<th>HTM and its deposition method</th>
<th>Back electrode</th>
<th>η (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-PEN</td>
<td>n-i-p</td>
<td>ZnO – Spin coating</td>
<td>Spin coating</td>
<td>PTAA- Spin coating</td>
<td>Gold</td>
<td>15.6</td>
<td>Heo et al 2016</td>
</tr>
<tr>
<td>ITO-PET</td>
<td>p-i-n</td>
<td>PCBM</td>
<td>Spin coating</td>
<td>NiO</td>
<td>Ag</td>
<td>14.5</td>
<td>Docampo et al 2013</td>
</tr>
<tr>
<td>PET</td>
<td>TCO-free p-i-n</td>
<td>PCBM</td>
<td>Spin coating</td>
<td>PEDOT:PSS</td>
<td>Al</td>
<td>14</td>
<td>Li et al 2016</td>
</tr>
<tr>
<td>Metal Titanium</td>
<td>p-i-n</td>
<td>Titanium nanowires</td>
<td>Infiltration</td>
<td>PEDOT</td>
<td>ITO-PEN</td>
<td>13.1</td>
<td>Xiao et al 2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrothermal synthesis</td>
<td></td>
<td></td>
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</tbody>
</table>

5. Dye-sensitized solar cell textiles

Making solar cells not only from lightweight and flexible, but also stretchable, conformable and breathable materials that could be woven or knitted like common textiles, has stimulated the curiosity and inventiveness of researchers for long.

Photovoltaic textiles can be fabricated mainly via three different approaches: (1) attaching separate rigid or flexible solar cells onto textile fabrics, (2) coating an already formed textile with the solar cell materials, or (3) weaving or knitting fibers that have been rendered photovoltaic by deposition of solar
cell materials on them (Mather and Wilson 2017). In the first approach, an already functional solar cell is simply laminated or glued to the surface of a fabric. Although this can in many cases be the most feasible, efficient and durable solution to implement photovoltaic function to a fabric, the result can hardly be considered as a true photovoltaic textile, as the solar cell part itself lacks at least some of the above-mentioned properties that makes textiles superior to plastic or metallic foils in many applications.

In the second approach, where a solar cell is fabricated on a pre-existing woven, non-woven or mesh-like, porous textile, the textile serves as a structural or functional part of the solar cell device, bringing the idea closer to an actual photovoltaic textile. However, because all solar cells need some kind of encapsulation to reach adequate durability at use, the resulting structure is often quite similar to the first approach, except perhaps thinner and more flexible (Opwis et al 2016).

From the stand-point of intimate photovoltaic-textile-integration, the third approach, where individual fiber-like solar cells are assembled together by knitting, weaving and sewing techniques to form a functional structure, is perhaps most intriguing and has stimulated researchers attention (Peng and Zou 2015). However, most of the studies in this front have focused on individual solar cell wires or fibers, e.g. Qiu et al (2016) and Li et al (2015), or have reported at best only very basic textile-like arrangements, e.g. Qiu et al (2014) and Yang et al (2014), or individual tubular cells sewn on the textile, e.g. Pu et al (2016). It is therefore still unclear, how closely these fiber-like solar cells could reproduce the functional characteristics of common textiles that serve as their point of reference and inspiration.

A fourth approach (4) is the case where the photovoltaic functionality arises from knitting, weaving or sewing together threads, tapes or wires made of different materials, each having a specific sub-functionality, e.g. photoelectrode, counter electrode, conductor, and separator wires. This approach has been the most common one with DSCs.

In the following, we review examples from recent literature on the application of industrially relevant weaving, knitting and sewing processes for the fabrication of textile structures with dye-sensitized solar cell functionality. No examples of textile-like perovskite solar cells were found; only single fiber PSCs seems to have been reported so far, e.g. Qiu et al (2014), Li et al (2015), and Qiu et al (2016). We omit also papers that report fiber-like DSCs without forming textile structures from them, papers where textile materials have been used only as one part of the cell, enclosed inside an otherwise non-textile-like solar cell (approaches 1 and 2 above), and papers where the woven solar cell strips have been clearly too large to be considered as serious textile components, e.g. Li et al (2016). The review focuses
on the used materials, fabrication processes, and structures and the photovoltaic performance obtained.

**DSC textiles with volatile liquid electrolyte**

As already mentioned, the ultimate goal would be a photovoltaic textile fiber that could be woven or knitted into textile structure using existing industrially applicable textile production processes. Yun et al. (2014) presented a step towards this direction, reporting multi-layered liquid-electrolyte DSCs fabricated by sewing textile-structured electrodes, and reaching ca. 5.8 % efficiency (Figure 5 a-c). The electrodes consisted of TiO$_2$ sensitized with N719 dye (photoelectrode) and Pt (counter electrode) deposited onto textile layer that combined perforated stainless-steel ribbons as the weft and Ti wire (0.1 mm) as the warp. At the edge region, glass fibers replaced the steel ribbons as wefts, which allowed sewing the PE and CE textiles together using a porous insulating textile cloth (cotton, silk, or paper) as a separator. The steel ribbons provided a relatively flat surface for the TiO$_2$ and Pt layers deposited by doctor-blading and screen-printing, whereas the use of heat-resistant materials (stainless steel, Ti and glass) allowed normal high-temperature treatment of the TiO$_2$ and Pt layers. The cells had TCO-free back-contact device geometry and were 0.7-0.8 mm thick after sewing. Some of the mentioned problems limiting the performance were low porosity of the separator layer, loss of contact between the PE and CE textile layers, and evaporation of the acetonitrile-based electrolyte.

Later Yun et al. reported several other types of textile DSC designs following the above approach and using N719 dye. In Yun et al (2015), the authors improved their previous structure mechanically by using Pt-coated carbon yarn as the CE weft and textile warps as spacers to better maintain the device structure (Figure 5 d-f). The cells, heat-sealed inside a PET laminate pouch, reached 2.63 % efficiency using an acetonitrile-based electrolyte. In Yun et al (2016a), the authors simplified the structure by weaving parallel Pt-coated Ti wires and bare Ti wires with glass yarns to produce a single-layer textile DSC, where a high-temperature-sintered TiO$_2$ layer covered the whole underlying textile structure in a monolithic manner (Figure 5 g-i). The cells were unstable, losing 50 % of their efficiency in seven days due to evaporation of the acetonitrile-based electrolyte. The same team also studied and optimized the printing process for metal mesh substrates relevant to the fabrication of this type of textile DSCs, and reached 4.16 % efficiency for a cell that had 3-methoxypropionitrile-based liquid electrolyte (Yun et al 2016b). In this case, the cell was not a part of a larger textile structure, but a separate device encapsulated inside PET/EVA plastic.
Figure 5. Examples of woven DSC textile structures based on conventional DSC materials (TiO$_2$, Ti, stainless steel, glass, N719 dye, and volatile liquid electrolyte) by Yun et al. (Yun et al. 2014): (a) Cross-section of the woven structure. Note how the PE and CE sides were sewn together through a non-active glass-fiber-woven part of the textile; (b) An open textile DSC before adding electrolyte; (c) Complete, encapsulated textile DSC. (Yun et al. 2015): (d) A woven textile DSC design based on perforated metal ribbons, (e) its cross-section, and (f) photograph; (Yun et al. 2016a): (g) Textile DSC design based on parallel PE and CE electrode wires; (h) its cross-section, and (i) photograph. Reproduced by permission from Nature Publishing Group (Copyright).

**Solid-state DSC textiles based on Cul hole-conductor**

Zhang et al (2016) demonstrated a step towards solid-state textile DSC by using Cul as hole-conductor (Figure 6a-b). The authors weaved strings of wire-shaped photoelectrode and counter electrode threads together in an interlaced manner to create a single layered textile. The cells had dye-sensitized ZnO nanoarray photoelectrodes (N719 dye) deposited on Mn-plated polybutylene terephthalate (PBT) polymer wires with 0.26 mm diameter. The PE wires were coated with the Cul hole-transport material and interlaced with Cu wires (0.05 – 0.21 mm diameter) that served as the counter electrode threads (Figure 6). The structure was TCO-free, which is common in the literature for textile- and fiber-like DSC, and often necessary for adequate conductivity and flexing durability. The cells reached 1.3 % efficiency and 7.8 mA cm$^{-2}$ short-circuit current density at a single cell level, measured at 1 Sun conditions and
calculated per projected, i.e. effective, shadow-casting, area of the device. Systematic characterization of the effect of different weaving patterns and electrical connection schemes on the photovoltaic performance of the DSC textile showed that its output current and voltage was designable by connecting the strings in series and parallel as needed. The Cu-wire CEs caused significant shading losses on the PE string, which was managed by optimizing the weaving pattern.

Chai et al (2016) combined the above CuI solid-state DSC textiles and fiber supercapacitors in a single woven structure to form a combined energy harvesting and storage textile (Figure 6c-d). In this case, Cu-coated polymer wires or cotton yarns served as the counter electrodes threads. The solar cells had 0.9% efficiency, but the area definition was not mentioned. The textile DSC endured short term bending tests and was stable for more than two months when stored in dry conditions without encapsulation. The solar cell electrodes were woven together with fiber supercapacitors using cotton yarns. The supercapacitors consisted of two parallel Ti wires (0.25 mm diameter) with grown TiN nanowire array electrode that was covered with thin amorphous carbon shell. The parallel electrode wires were surrounded by KOH/PVA gel electrolyte (0.8 mm diameter) that served also as a spacer between them (Figure 6). The combined textile sample charged to 1.2 V in 17 s under illumination and discharged fully in 78 s in the dark at 0.1 mA discharge current.

Chen et al (2016) weaved the CuI solid-state DSC wires with triboelectric generator (TEG) electrodes made from 30 µm thick and 0.3 mm wide strips of Cu foils sandwiched between two 33 µm thick polytetrafluoroethylene layers, to make a combined light and mechanical energy harvesting textile (Figure 6 e-f). The electrodes were woven into plain, twill and satin patterns with an industrial weaving machine. Cu-coated PBT wires served as counter electrodes for both the DSC and TEG parts. The textile DSCs had short-circuit current density between 5.8 mA cm⁻² and 6.35 mA cm⁻², and less than 0.9% efficiency, calculated per projected area of the photoelectrodes. The DSC and TENG components had complementary power output vs. load resistance characteristics and worked successfully in several practical application demonstrations.

Discussion

The above examples demonstrate two strategically different approaches to textile DSCs. The approach of Yun et al (2014, 2015, 2016a, 2016b), represents a systematic attempt to accommodate conventional DSC materials (TiO₂, Ti, stainless steel, glass, N719 dye, volatile liquid electrolyte) and fabrication processes (e.g. high-temperature sintering) in highly sophisticated textile structures fabricated by
weaving and sewing. Thanks to use of conventional DSC materials the cell efficiencies were relatively high (2.68 – 5.8 %), but this came at the cost of poor device stability due to evaporation of the electrolyte. Solid-state DSCs, an approach followed by another research group (Zhang et al 2016), (Chai et al 2016), (Chen et al 2016), mitigates the electrolyte volatility and encapsulation problems, demonstrating reasonable stability at least at dry conditions, but this comes at the cost of efficiency that was 1.3 % at best.

Figure 6. Examples of solid-state DSC textiles based on CuI hole-conductor: (a) Basic woven structure of the solid-state textile DSC, and (b) an example where it has been woven together with common textile material (Zhang et al 2016). (c-f) The same solar cell structure woven on the same textile piece with (c) fiber super-capacitors (Chai et al 2016) and (e) triboelectric generators (Chen et al 2016), and their practical demonstrations (d, f). Reproduced by permission from American Chemical Society (Copyright), Nature Publishing Group (Copyright), John Wiley and Sons (Copyright).

The reviewed results shown that establishing facile charge transport and secure encapsulation are one of the biggest challenges in realizing practically relevant DSC textiles. Krebs and Hösel (2015) came to a similar conclusion when assessing the feasibility of polymer solar cell textiles. Considering additionally the mechanical requirements that industrial textile manufacturing processes present to the durability of the fiber materials used, and many other practical aspects, they concluded that weaving separate tape-like solar cells with common textile materials would be the most feasible approach to photovoltaic textiles. Indeed, tape weaving appears to be a good compromise between the two worlds: narrow solar cells strips can provide flexibility in one direction, whereas weaving them together with flexible or stretchable fibers adds conformability also in the other direction on the textile plane (Figure 7). At
present, however, the textile DSCs reported in the literature and discussed above are quite far from practical applications, at least when it comes to wearable textiles. Instead of trying to miniaturize bulky solar cells to thin fibers that would be required for plausible replacement of common textile fibers, a more fruitful goal could be to go to the opposite direction, pointed out by Krebs and Hösel (2015), namely, to use textile-manufacturing processes as means to scale-up the device area of roll-to-roll-printed solar cells.

6. Stability aspects of flexible DSC and PSC

A substrate does not only provide mechanical support to the functional material layers of a solar cell, but also affects its stability in the long-term. An appropriate substrate functions as an encapsulant that protects the cell against the intrusion of unwanted contaminants and moisture into the cell. The degradation mechanisms in DSCs (Asghar et al 2010, Asghar and Lund 2016) and PSCs (Asghar et al 2017) due to these contaminants have been reported in detail in the literature. As an example, failure of a substrate could result in penetration of moisture in the cell, which could lead to severe degradation of the light absorber in the cell. Following reactions show degradation through dissociation of the light absorber in a PSC due to presence of moisture in the cell (Asghar et al 2017):

Figure 7. a) Structure of the tape-weaved solar cell textile reported by Krebs and Hösel (2015), and b) a photograph of one of their large area (25 x 25 cm²) solar cell textile examples. The solar tapes weaved in the structure consisted of 16 serially connected single junction organic solar cells and had an active area of 368 cm² and efficiency of ca. 1%. Reproduced with permission from John Wiley and Sons (copyright).
$4\text{CH}_3\text{NH}_3\text{PbI}_3 \xleftrightarrow{H_2O} 4[\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot H_2O]$  

$4[\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot H_2O] \xleftrightarrow{H_2O} (\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2H_2O + 3\text{PbI}_2$

A substrate should ideally meet a set of requirements, which are required for a durable solar cell. The stability of solar cells is evaluated through certain criteria that include standard accelerated aging tests under different stress conditions (UV-vis light exposure, heat, humidity and mechanical force). More details of these accelerated aging tests and their protocols for thin film solar cells (IEC 61646) can be found from Osterwald and McMahon (2009). In case of a flexible solar cell, the substrate should also support the deposited films to pass a bending cyclic test. Although, there is no standard bending test for the solar cells, the commonly used bending tests give an indication of the stability of the substrates and the thin films deposited on top of them. In flexible hybrid electronic industry, the ASTM D522M is a standard to test the organic coatings onto the flexible substrates (Hackler et al 2017). However, in photovoltaic community researchers commonly use different bending radius and number of cycles to demonstrate the stability of their flexible solar cells. The smaller the bending radius, the more the substrate and the films would be under mechanical stress due to larger degree of bending.

The chemical nature of a substrate limits the process conditions, e.g. sintering temperature, required for the manufacturing of a solar cell, thus affecting its stability. For instance, most of the plastic substrates are not suitable for heat treatment over 180°C. The heat treatments of the two most commonly used plastic substrates in DSC and PSC applications, i.e. ITO-PET and ITO-PEN, are limited to 150°C and 180°C, respectively. Therefore, the films deposited on these substrates cannot be sintered for higher temperature, which may result in faster degradation of the films. Although, plastic substrates are an attractive option due to their lightweight and suitability for large scale roll to roll production, they are permeable to water and oxygen. The intrusion of these unwanted impurities are detrimental to the device stability (Asghar et al 2010, 2017). Furthermore, the volatile electrolyte solvents in the cell electrolyte are prone to escape through these permeable substrates (Asghar et al 2010, 2017). Therefore, a plastic substrate can affect both the intrinsic (degradation due to internal factors) and extrinsic (degradation due to external factors) stability of a solar cell. That is one of the reason that the best stability results are obtained with glass based TCO substrates (ITO, FTO, etc.) because it caters stability issues of both intrinsic and extrinsic nature, i.e. they allow high temperature sintering (450°C) for the deposited films and also block the unwanted contaminants from the environment (Asghar et al
2010, 2017). The glass based DSCs mainly degrade due to detrimental interactions between the cell components, e.g. resulting bleaching of the cell color, and failure of the sealant (Mastroianni et al 2014, Asghar et al 2012, Andersen et al 2011). The interactions between the electrolyte and dye have been investigated in detail in our previous study (Asghar et al 2016, Jeanbourquin et al 2014, Rendon et al 2015). The glass substrate remains inert throughout the lifetime of the cell. However, unfortunately due to the rigidness of the glass substrates, the solar cells lose their flexibility feature.

A flexible metal substrate (Ti, stainless steel, etc.) is a good solution as it functions as an efficient encapsulant and also withstands the high temperature treatments required for producing stable functional films in a solar cell. Interfaces between the metal substrate and the electrolyte or electrode are crucial for the stability of a solar cell. Several metal substrates including stainless steels 304 and 321, and acid proof steels 316 and 316L have been reported to degrade at the photoelectrode (Miettunen et al 2010). On the counter electrode side stainless steels 304 and 321, acid proof steel 316, and Inconel 600 are prone to corrosion (Miettunen et al 2011, Asghar and Lund 2016). Interestingly, the Inconel substrate and acid proof steel 316L were found to be quite stable at photoelectrode and counter electrode, respectively (Miettunen et al 2010, Miettunen et al 2011). Ti was the only metal that was found stable at both photoelectrode and counter electrode without using any protective barrier layer (Miettunen et al 2010, Miettunen et al 2011). All these metal substrates, except inconel 600, have been successfully prevented from corrosion by depositing a thin sputtered platinum film at the counter electrode (Miettunen et al 2011, Asghar and Lund 2016).

Whilst the degradation processes with both metal photoelectrode and counter electrodes show differences (Miettunen et al 2013a), it is clear that corrosion plays a much bigger role than initially anticipated (Miettunen et al 2015): A puzzling question for many years was why the conventional corrosion tests predicted metals to be stable in electrolytes, but when the metals were applied in working devices most of them failed (Miettunen et al 2013a). The reason was that the metal cells stopped working not because the metal substrate was too damaged (factor that the conventional tests investigate), but because the cell ran out of charge carriers which act as the corroding agent (Miettunen et al 2015).

As an example, the corrosion reaction of an iron substrate with the tri-iodide is given below:

\[ \text{Fe} + \text{I}_3^- \rightarrow \text{Fe}^{2+} + 3\text{I}^- \]
Typically the amount of charge carriers in a cell run out about 10,000 times more quickly than the time needed to result in a major damage to the metal (Miettunen et al 2015) and thus the metals need to be highly resistive towards corrosion. Even such electrolytes that were deemed completely non-corrosive, such as cobalt complex electrolytes, did corrode many metals, but some cheaper and stable alternatives were found, e.g. ferritic steel (Miettunen et al 2013b, Miettunen et al 2014). Despite these challenges, both good performing metal and plastic substrates have been reported as shown in the Table 2, and therefore a stable combination of a flexible solar cell could be a metal-based photoelectrode and a plastic based counter electrode.

Table 2. State of the art of stability of flexible dye solar cells.

<table>
<thead>
<tr>
<th>Substrate at photoelectrode</th>
<th>Substrate at counter electrode</th>
<th>Initial $\eta$ (%)</th>
<th>Test condition</th>
<th>Stability result (efficiency loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-PEN</td>
<td>ITO-PET</td>
<td>4.0</td>
<td>1000 h aging at 60°C under 1 Sun illumination</td>
<td>&lt;10% (Han et al 2015)</td>
</tr>
<tr>
<td>ITO-PET</td>
<td>No substrate, Au is used as current collector</td>
<td>9.4</td>
<td>AM1.5G 100 mW/cm$^2$ illumination</td>
<td>&lt;5% (Zhang et al 2017)</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>ITO-PEN</td>
<td>2.0</td>
<td>1000 h aging at 60°C under 1 Sun illumination</td>
<td>No loss (Lee et al 2011)</td>
</tr>
<tr>
<td>Ti foil</td>
<td>ITO-PEN</td>
<td>5.0</td>
<td>3120 hours aging in dark</td>
<td>&lt;10% (Jen et al 2013)</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>ITO-PET</td>
<td>3.42</td>
<td>100 bending cycles (bending R not reported)</td>
<td>&lt;15% (Drygala et al 2017)</td>
</tr>
<tr>
<td>Substrate</td>
<td>PSC configuration</td>
<td>Initial $\eta$ (%)</td>
<td>Test condition</td>
<td>Stability result (efficiency loss)</td>
</tr>
<tr>
<td>-----------</td>
<td>------------------</td>
<td>------------------</td>
<td>----------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>Inverted planar</td>
<td>14.7</td>
<td>600 bending cycles with a radius of 20 mm, 15 mm, 10 mm, 8 mm and 4 mm respectively</td>
<td>&lt;2% (Jo et al 2016) &lt;2% (Jo et al 2016) &lt;5% (Jo et al 2016) &lt;30% (Jo et al 2016) &lt;50% (Jo et al 2016)</td>
</tr>
<tr>
<td>ITO-PEN</td>
<td>Planar</td>
<td>15.3</td>
<td>300 bending cycles (bending radius is not reported)</td>
<td>&lt;5% (Shin et al 2015)</td>
</tr>
<tr>
<td>Ultra-thin flexible glass</td>
<td>Inverted planar</td>
<td>11.7</td>
<td>200 bending cycles with a bending radius of 4 cm</td>
<td>&lt;5% (Tavakoli et al 2015)</td>
</tr>
<tr>
<td>ITO-PET</td>
<td>Planar</td>
<td>~15</td>
<td>200 bending cycles with a bending radius of 10 mm</td>
<td>&lt;20% (Mali et al 2017)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.6</td>
<td>600 bending cycles with a bending radius of 10 mm and 15 mm</td>
<td>&lt;10% (Jung et al 2017)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.7</td>
<td></td>
<td>&lt;5% (Jung et al 2017)</td>
</tr>
</tbody>
</table>

Stable photodeode in a dye solar cell using a plastic substrate has been fabricated through a cold isostatic pressing method (Weerasinghe et al 2012), which is a powder compaction technique. It produced TiO$_2$ films with both the high mechanical stability and electrical conductivity. This outstanding finding allows using the plastic based photodeodees with the metal-based counter electrodes. Furthermore, it enables to produce a semitransparent flexible solar cell using plastic substrates at both the photodeode and counter electrode. Tables 2&3 present the state of the art of stability of flexible dye-sensitized and perovskite solar cells, respectively.
7. Conclusions

Flexible substrates represent future directions in photovoltaics (PV) technology. Flexibility would be particularly relevant for next generation PV, in which material needs for photoactive layers are low and which are suitable for roll-to-roll and advanced manufacturing processes.

In this review, we focused on dye-sensitized (DSC) and perovskite (PSC) solar cells with flexible substrates. Commonly employed materials include polymeric materials or plastics (ITO-PEN, ITO-PET) and metallic foils (stainless-steel, titanium). These are not yet well commercially established and are still in a development phase. We also reviewed the use of textiles/clothes as substrates, which could be relevant for personal energy harvesting applications or a way to scale-up the device area of roll-to-roll produced flexible solar modules.

Typically at this stage of development, employing a flexible substrate would yield lower conversion efficiency than with a glass substrate, mainly because of different charge loss mechanisms. Highest efficiencies reported for flexible DSC is almost up to 10% and for PSC 15%, which falls short some 30% from the highest reported values for these types of solar cells. Another major challenge is the cell stability over time, which suffers from degradation mechanisms caused by humidity and corrosion, among others. Mechanical stability is already at a quite good stand.

Future development of flexible DSC and PSC includes increasing overall lifetime and cell efficiency. Scaling up of modules to size of practical relevance for major applications, e.g. in building integration, is also of high future interest.

Acknowledgements

The financial support from the Kone Foundation and Academy of Finland project #287641 is gratefully acknowledged.
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