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Abstract

A porous, flexible electrode based on a PTFE (Teflon) membrane (Goretex) coated with a metallic current collector and a conducting polymer (poly(3,4-ethylenedioxythiophene), PEDOT) has been developed for applications in solidstate dye-sensitized solar cells. Its low sheet resistance and compressibility make it an ideal electrode on uneven TiO₂ surfaces with high efficiency and reproducibility. The porous nature of the electrode enables the feed-through of reactants and treatment agents, which opens up exciting opportunities to interface these photoelectrochemical devices with electrocatalytic, energy conversion, and storage systems. Postfabrication bonding of the photoanode and the Goretex-Au-PEDOT electrode is demonstrated.

Keywords

flexible, electrodes, pedot, membrane, compressible, goretex, sensitized, solar, dye, cells, solid, state

Disciplines

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Flexible and Compressible Goretex—PEDOT Membrane Electrodes for Solid-State Dye-Sensitized Solar Cells

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A porous, flexible electrode based on a PTFE (Teflon) membrane (Goretex) coated with a metallic current collector and a conducting polymer (poly(3,4-ethylenedioxythiophene), PEDOT) has been developed for applications in solid-state dye-sensitized solar cells. Its low sheet resistance and compressibility make it an ideal electrode on uneven TiO₂ surfaces with high efficiency and reproducibility. The porous nature of the electrode enables the feed-through of reactants and treatment agents, which opens up exciting opportunities to interface these photoelectrochemical devices with electrocatalytic, energy conversion, and storage systems. Postfabrication bonding of the photoanode and the Goretex—Au—PEDOT electrode is demonstrated.

Solid-state dye-sensitized solar cells^{1,2} (sDSSC) consist of a light-absorbing pigment chemically attached to a nanostructured TiO₂ layer impregnated with a solid-state hole conductor providing electrical contact between the pigment molecules and the current collector electrode. The best performing sDSSC reaches 5% power conversion efficiency³ (η) and uses small-molecule hole conductor spiro-OMeTAD (2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spiro-bifluorene) deposited using conventional solution processing techniques. A major barrier toward improved efficiency is the optimization of the pore filling of the TiO₂ photoanode.⁴ An alternative photoelectrochemical method in which an electroactive hole conducting polymer (polypyrrole) is deposited in situ within the pores of the photoanode was proposed by Yanagida et al.⁵ Optimization of the deposition conditions and subsequent ionic liquid treatment have recently resulted in $\eta = 2.8\%$.⁶ Physical pore filling, where the hole conductor is dissolved in a suitable solvent and introduced into the pores, relies on capillary forces and gravity. The photoelectrochemical method, which prepares the hole conductor in situ adjacent to the dye molecules where it is needed, gives additional control over pore filling by tuning the light intensity⁷ and illumination side.⁸ One of the shortcomings of this solar cell is that the currently used sputtered gold or platinum on an ITO current collector lacks reproducibility in our laboratory: the shape of the current—voltage curves strongly depends on the ability to

apply a reproducible force that holds the two rigid, noncompressible electrodes together. To achieve good physical contact between two noncompressible electrodes, TiO₂ needs to be defect-free and perfectly even over a large surface area. Moreover, the best performing configuration of this cell requires a post-fabrication ionic liquid treatment that improves the conductivity of the photoelectrochemically deposited PEDOT.⁶ A commonly used current-collecting electrode for solid-state organic solar cells consists of a thin (20 to 100 nm) evaporated metal contact (e.g., Au or Ag for sDSSC's). As will be demonstrated below, these evaporated electrodes do not perform well for the sDSSC's developed here. First, evaporated/sputtered Au is known to diffuse into soft organic layers, causing electrical shorts and possible degradation of the organics. Second, the photoanode needs to be flat on the 20 to 100 nm scale and free of major defects, which would reduce the actual contact surface area or lead to low conductivity of the evaporated contact. Finally, a perfectly flat, evaporated Au contact is expected to be nonporous, which limits its applicability if postdeposition treatment is required for high performance.

With this in mind, we have set a number of requirements that an ideal current-collector electrode needs to fulfill: It should be fully flexible, compressible, conformal, and highly conductive on the basis of readily available, cost-effective, durable materials. Furthermore, the electrode should be porous, allowing the feed-through of treating agents. As will be demonstrated below, we have developed a novel porous membrane electrode that fulfills these requirements based on a well-known Goretex membrane. One side of the Goretex membrane is coated with ~10 nm poly(maleic anhydride) using low-power plasma polymerization⁹ and afterwards sputter coated with a 40 nm layer of Au, reducing the sheet resistance. We used Au initially, but this can be replaced by a nonprecious metal such as titanium or nickel. The combined Au and plasma-polymerized layer prevents the membrane from being flooded by the 40% Fe(III)PTS solution in butanol used as

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Figure 1. (A) Schematic representation and layer structure of a solid-state dye-sensitized solar cell using photoelectrochemically deposited PEDOT as a hole conductor. SEM images of (B) the Goretex–Au–PEDOT cross-section and the photoanode surface (C) after and (D) before PEDOT deposition.

an oxidant for the vapor-phase polymerization¹⁰ of PEDOT, thus allowing coating with PEDOT on only one side of the membrane.¹¹ The thickness of the PEDOT layers produced by this method has been measured by SEM (of the electrode cross section) to be in the 400–500 nm range. This membrane construction has proven to be permeable for gases but impermeable for aqueous electrolytes, providing an efficient three-phase interface for oxygen reduction.¹¹ The conducting coating has a sheet resistance of around 6 Ω /square. It is well bonded to the membrane, which makes the construction very durable and flexible with respect to following the bending of the membrane. Goretex membranes are known to be wettable¹² by nonaqueous solvents such as ethanol, and the same is the case for the Au–PEDOT-coated membrane, allowing feed-through of species such as sensitizing dyes, monomers, and electrolytes soluble in suitable solvents.

The architecture of the solid-state dye solar cells is shown in Figure 1A. The cross section of the Goretex–Au–PEDOT membrane (Figure 1B) and the surface of the photoanode after (Figure 1C) and before (Figure 1D) the photoelectrochemical deposition of PEDOT imaged using SEM are also displayed. The photoanode was prepared by a published photoelectrochemical method (SI 1).¹³ The SEM image of the photoanode 30 min after PEDOT deposition indicates that the pores of the TiO₂ electrode are partially filled with PEDOT. Note that with current-optimized procedures the photoelectrochemical growth of PEDOT stops after 30 min; therefore, this represents the maximum amount that we can currently grow. A thin, noncontinuous polymer film is formed on the surface of the photoanode. To estimate the total amount of PEDOT within the pores of the TiO₂ electrode, we have measured its UV–vis and near-IR absorption, which is comparable in magnitude to the absorption

Figure 2. Surface profiles of (a) bare FTO glass, (b) sputtered Au on ITO glass, (c) the TiO₂ photoanode incorporating sensitizing dye and photoelectrochemically deposited PEDOT, and (d) the Goretex–Au–PEDOT membrane. The TiO₂ photoanode scan (c) was leveled to the underlying FTO glass on each side. The surface profiles were offset from each other for better viewing.

by the dye layer. Using the known absorption coefficient of PEDOT,¹⁴ we have estimated (see the detailed calculation in SI 2) that the photoelectrochemically deposited PEDOT amounts to a total film thickness of around 100 nm. It is clear from the efficient photovoltaic response of these devices that this total 100 nm is distributed, although not uniformly, within the pores of a 5 μ m TiO₂ film, and there is only a rather thin (< 20 nm, see cross-sectional SEM images in SI 6) PEDOT film on the surface of the photoanode. Because of the morphology of the films, evaporating/sputtering Au on the top of these photoanodes as a simple and commonly used method is not effective due to migration of Au through the thin polymer layer causing electrical shorts and possible degradation of the organic layers.¹⁵

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AFM images of Goretex–Au–PEDOT (shown in SI 4) reveal that the roughness measured on a small scale (1 μm scan) is comparable to that of the TiO_2 layer. However, good contact between TiO_2 and the counter electrode is also dependent on the roughness and therefore possible contact points on a larger scale. Figure 2a,b displays surface profiles of FTO and sputtered Au/ITO electrodes; meanwhile, Figure 2c displays a TiO_2 film incorporating the sensitizing dye and photoelectrochemically deposited PEDOT. The surface profile of the TiO_2 layer is leveled to the underlying FTO substrate; therefore, the slope in Figure 2c is due to a rather large variation of the thickness of the electrode. Such an uneven TiO_2 photoanode was selected to demonstrate the clear advantage of the flexible and compressible Goretex–Au–PEDOT electrodes. The current–voltage curves measured under a 100 mW cm^{-2} calibrated air mass with 1.5 illumination of the sDSSC's comprising the same photoanode and sputtered Au on an ITO electrode (thin line) or the novel Goretex–Au–PEDOT membrane (thick line), are shown in Figure 3. Approximately a 3 times higher (2.85%) power conversion efficiency is achieved using our novel electrode as compared to the commonly used flat, rigid Au–ITO glass (0.85%), and it is also significantly higher than a Au electrode evaporated directly on top of the photoanode (0.5%). We note that by using a flat, defect-free photoanode the best efficiency of $\eta = 2.9\%$ has been

Figure 3. Current density vs voltage curves measured for solid-state dye solar cells using sputtered Au/ITO (thin line) and a Goretex–Au–PEDOT (thick line) electrode under AM1.5 G illumination (continuous line) and in the dark (dashed line).

achieved in our laboratory using Au–ITO, which is to our knowledge the highest reported current for photoelectrochemically deposited PEDOT using Z907 dye, providing a state-of-the-art comparison to the various electrodes presented here.

It is clear that forming a direct contact to such an uneven TiO_2 film with defects using a rigid, incompressible FTO or gold/ITO electrode is very difficult, giving only a few contact points, which is manifested in a low filling (0.38) and short circuit current (3.5 mA cm^{-2}). In comparison, 0.65 and 6.7 mA cm^{-2} were achieved using the same TiO_2 photoanode and the compressible Goretex–Au–PEDOT electrode. The PEDOT coated onto Au–Goretex (Figure 2d) appears to have a much rougher surface than that of the TiO_2 photoanode on the macroscopic scale (average surface roughness, R_a , for Goretex–Au–PEDOT is about 3 times higher than for the TiO_2 photoanodes; see Table 1). The number of contact points when combined with the TiO_2 electrode, however, will be much higher than for a rigid electrode such as FTO or ITO if the compressibility and flexibility of the Goretex–Au–PEDOT are taken into account. The compressibility of the $80\text{-}\mu\text{m}$ -thick Goretex–Au–PEDOT electrode was measured to be 60%, which is in good agreement with the specification from the supplier ($>55\%$) for bare Goretex. The force required to compress the electrode is very small: the first $10\text{ }\mu\text{m}$ of deformation requires only 10 mN/mm^2 (SI 3). The maximum height of the defect features on the TiO_2 surface (Figure 2d) are in the $2\text{ }\mu\text{m}$ range, which can easily be compensated for by the Goretex–Au–PEDOT electrode, ensuring good electrical contact between the two parts of the cell.

We have experimented with a number of rigid or flexible electrodes using sputtered metals or vapor-phase-polymerized PEDOT as current-collecting electrodes. The results for these electrodes using either (I) even or (II) uneven or otherwise identically prepared TiO_2 photoanodes are compared in Table 1. The maximum performance of around 2.85% can be achieved with various electrodes on a defect-free photoanode, including ITO, Au–ITO, Au–Mylar and the novel Goretex–Au–PEDOT electrode. As published by us and others, this current performance of $\sim 2.85\%$ is limited by the incomplete filling of the pores of the photoanode. Further improvements are expected by obtaining a complete morphological map that will provide a thorough understanding of the photoelectrochemical growth of PEDOT within the pores. The novelty of the new Goretex–Au–PEDOT electrode is that this high efficiency can be achieved independently of the variation of the TiO_2 film quality.

Table 1. Photovoltaic Properties of Solid-State Dye-Sensitized Solar Cells Using Various Current-Collecting Electrodes

counter electrodes ^a	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η (%)	resistance (Ω/square)	R_a (nm) ^c	max dev (nm) ^c
ITO (I)	795	6.11	0.58	2.81	7	5	25
FTO (I)	760	5.85	0.47	2.10	9	8	67
Pt/ITO (I)	755	6.78	0.42	2.14	10	6	17
Au/ITO (I)	755	6.88	0.40	2.06	2	3	27
PEDOT/Au–Mylar (I)	640	6.59	0.68	2.89	2	280	1840
PEDOT/Ti (I)	610	6.28	0.54	2.07	<1	200	1270
PEDOT/Ti/Kapton (I)	625	5.49	0.44	1.51	12	220	1170
Au/ITO (II)	635	3.5	0.38	0.85	2	3	27
PEDOT/Au/Goretex (II)	655	6.70	0.65	2.85	6	290	900
evaporated Au (II)	505	2	0.51	0.5	N.A.	<i>d</i>	<i>d</i>
AU/ITO (I), BEST	725	6.02	0.66	2.89	2	3	27
$\text{TiO}_2/\text{dye}/\text{PEDOT}$ (II) ^b						90 (± 40) nm	2700 (± 1400) nm

^a (I) A defect-free photoanode is used. (II) An uneven photoanode (surface profile exhibited in Figure 2) is used. ^b An average of four samples was calculated. A single scan was performed in the middle of a $5\text{ mm} \times 6\text{ mm}$ film area. ^c Calculated on a $1\text{--}5\text{ mm}$ scale. ^d Au is evaporated on top of a $\text{TiO}_2/\text{dye}/\text{PEDOT}$ electrode; therefore, R_a and max dev are nearly identical to those for the $\text{TiO}_2/\text{dye}/\text{PEDOT}$ layer.

Figure 4. (A) Current vs time during the postfabrication deposition of PEDOT through the Goretex–Au–PEDOT electrode. (B) Image of the photoanode after delamination of the bonded Goretex–Au–PEDOT electrode. (C) Image of the photoanode before postfabrication PEDOT deposition.

The average efficiency and standard variation of 8 devices prepared using the Goretex–Au–PEDOT electrode was $2.8 \pm 0.15\%$ as shown in SI 7.

In general, all of the electrodes have sufficiently low surface resistance and are expected to form an ohmic contact to the photoelectrochemically deposited PEDOT photoanode. The difference in their performance, therefore, cannot be explained by resistive losses. It is more likely to be related to the quality of the physical contact between the photoanode and current-collecting electrode, which depends on its surface roughness, porosity, and compressibility. Interestingly, the V_{oc} is 70 to 150 mV lower for all of the PEDOT-based electrodes, which may be related to its lower work function as compared to that for Au, Pt, ITO, or FTO.

Out of all of the electrodes displayed in Table 1, Goretex–Au–PEDOT provides an exciting feature that to our knowledge has not been explored in the literature. Its porous nature allows the feed-through of reactants, treating agents, or additional metal oxide precursors, opening up a range of novel fabrication possibilities. A simple one in which a permanent bond between the photoanode and the Goretex–Au–PEDOT electrode is achieved is demonstrated below. The Goretex–Au–PEDOT electrode was layered onto the photoanode. The photoanode and the Goretex–Au–PEDOT electrode were connected to a potentiostat, and 0.2 V was applied to the Goretex–Au–PEDOT. The measured current (Figure 4) slightly increased when the light was switched on after 1 min. After 2 min, a drop of bis-EDOT solution was

placed on the top of the membrane. As soon as the solution penetrated the membrane, an increase in the current was observed, indicating that a photoelectrochemical reaction was taking place. The current decreased after 5 min, which corresponds to the evaporation of the solvent. This procedure was repeated several times until PEDOT was fully formed between the two electrodes, creating a very strong bond. When the Goretex–Au–PEDOT was removed from the photoanode, a significant amount of PEDOT, as well as the sputtered Au deposited on the Goretex–Au–PEDOT electrode, was transferred to the photoanode side (Figure 4B), which indicates that the linkage between the photoanode and the vapor-phase polymerized Goretex–Au–PEDOT membrane is stronger than the Au–Goretex contact.

In summary, we have developed a compressible, flexible, highly conductive current-collecting electrode based on vapor-phase-polymerized PEDOT on a Au–Goretex membrane. Because of its 60% compressibility and 80% porosity, this novel electrode is tolerant of defects in the TiO₂ photoanode layer, which is expected to be beneficial for the large-scale, cost-effective, reproducible fabrication of next-generation solid-state organic solar cells. The Goretex–Au–PEDOT electrode is an important step toward wearable, textile-based photovoltaics that can be applied on uneven, curved surfaces. Finally, the permeability of the membrane opens up exciting opportunities to interface these light-harvesting devices with electrocatalytic, energy conversion, and storage devices.

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Supporting Information Available: Experimental details of the preparation of TiO₂/PEDOT photoanode and current-collecting electrodes, solar cell characterization, and surface profile measurements. UV–vis spectra of TiO₂/PEDOT electrodes. Compression versus force curve for a Goretex–PEDOT electrode. AFM images, surface profiles of the photoanode and Goretex–Au–PEDOT electrode, SEM cross-sectional images, and average and standard deviation of 8 randomly selected solid-state devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.