

Research article

Long-term investigation of unsealed DSSCs with glycerol-based electrolytes of different compositions

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Abstract: Long-term stability belongs to the main problems of dye-sensitized solar cells (DSSCs), impeding their practical application. Especially the usually fluid electrolyte tends to evaporation, thus drying the cells if they are not perfectly sealed. While gelling the electrolyte with different polymers often reduces the efficiency, using a glycerol-based electrolyte was already shown to result in similar or even improved efficiency. At the same time, drying of the cells was significantly reduced. Here we report on improving glycerol-based electrolytes further by varying the iodine-triiodide ratio and the overall concentration in the electrolyte. Long-term tests with unsealed glass-based DSSCs were performed over more than 1 year, showing that most of the cells increased efficiency during this time, opposite to cells with a commercial solvent-based iodine-triiodide electrolyte which completely dried after 2–3 months.

Keywords: dye-sensitized solar cells (DSSCs); glycerol; electrolyte; iodine-triiodide; natural dye; long-term study

1. Introduction

Dye-sensitized solar cells (DSSCs) have been investigated since their discovery 30 years ago [1] since they can be built from low-cost, nontoxic materials without the necessity to work in a cleanroom. Even natural dyes, typically derived from plants, can be used to prepare DSSCs, with the disadvantage, however, of relatively low efficiencies, typically below 1% [2–6], with few examples of efficiencies in the range of 2–4% [7,8]. On the other hand, working with inexpensive

materials allows for applying them on large areas, such as facades or textile architecture, e.g. tents.

It should be mentioned that using toxic ruthenium-based dyes, such as N719, or highly expensive dyes, such as N712, leads to significantly higher efficiencies. González-Verjan et al., e.g., report efficiencies of 4.0–6.4% using N719 combined with a nanoporous TiO₂ layer and I₂/LiI as electrolyte [9]. Subalakshmi and Senthilselvan also used N719 in their study of the effect of fluorine-doping of the TiO₂ photoanode, reaching 4.6–7.4% efficiency [10]. Investigating combustion synthesized TiO₂ as photoanode, Umale et al. also used N719 and reached an efficiency of 6.1% [11]. The effect of Pt-free metal sulfide counter electrodes was investigated by Subalakshmi et al. using N719, reporting an efficiency of 4.0% [12]. Patil et al. compared the 4N, N-dimethylaniline-based polyene sensitizers NKX-2553, NKX-2554, NKX-2600, and NKX-2569 theoretically with a frontier molecular orbitals approach and report values of 5–7% efficiency with unclear DSSC setup [13]. N712 dye is only scarcely found in the literature due to its high cost and reduced efficiency in comparison with N719. It should be mentioned that even higher efficiencies between 12% and 14% under simulated sunlight and even 29% under ambient light were reported in the literature; however, usually for only one or a few cells and without time-dependent measurements [14–17].

Another important issue to make DSSCs technologically applicable is their long-term stability. Most studies investigate maximum efficiencies, gained directly after production or few days afterward, when the efficiency is usually highest. Long-term investigations, on the other hand, often concentrate on the degradation of the dye [18,19], while especially for the possible application in textile architecture, a fluid electrolyte causes more problems [20]. Evaporation or drying of the electrolyte is typically counteracted by using gel-electrolytes or solid-state electrolytes [21–23], often based on poly (ethylene oxide) (PEO) with ionic conductivity [24,25]. Gelling or polymerizing the electrolyte aims at encapsulating the electrolyte to reduce leakage and evaporation [23,26–28]. Some groups carried out accelerated aging experiments to improve gel or solid-state electrolytes further in terms of long-term stability [29–33]. These gel- or solid-state polymer electrolytes, however, often suffer from reduced efficiency, as compared to common fluid electrolytes [28,34–36].

One of the materials which are sometimes included in gel- or solid-state electrolytes is glycerol. Glycerol has a very low vapor pressure and can thus be expected to show nearly no evaporation for long time. Recently, we showed long-term stability of a new glycerol/poly (ethylene oxide) polymer electrolyte during 75 days, however, with a relatively low efficiency around 0.002% [35]. Other groups used glycerol as a plasticizer to improve the ionic conductivity or generally the efficiency as compared to pure polymer based electrolytes [37–40], often only showing single measurements of the DSSCs so that long-term evaluations can rarely be found in the literature. Even less literature is available about glycerol as an addition to fluid electrolytes [41].

This is why in a previous project we suggested a glycerol-based electrolyte. Indeed, the first results showed significantly reduced electrolyte evaporation and constant efficiencies for more than four months or in several cases even increasing values during the time of the study [42]. Here, continuing this study, we investigate the influence of the iodine:triiodide ratio as well as the concentration of the electrolyte in the glycerol, showing values of more than 1 year of long-term examination.

2. Materials and methods

DSSCs were prepared using fluorine-doped tin oxide (FTO) coated glasses (Man Solar, Petten, The Netherlands) as front and back electrodes. All samples were prepared in triplicates. The front electrode had an additional TiO₂ layer of approximate thickness 6 μm , built from nanoparticles with typical diameters around 100–200 nm [43]. A graphite layer was coated onto the counter electrodes by pencil (J. S. Staedtler), supporting reentry of the electrons into the cells, returning from an external load.

Dyeing of the TiO₂ layer was performed with a forest fruit tea (Mayfair, Wilken Tee GmbH, Fulda, Germany) to enable comparison with the previous study. This tea contains anthocyanins which are used here as natural dyes. UV/Vis spectra of this tea can be found in Refs. [4,43,44]; transmission spectra of the pure TiO₂ coated electrode, the TiO₂ coated electrode with fresh and with old dye are depicted in Figure 1. The fresh dyed electrode shows a clear difference from the undyed TiO₂ around 550 nm, while the older dyed electrode has nearly fully lost its color and shows a transmission spectrum quite similar to the undyed TiO₂. The dyeing solution was prepared by mixing 2.5 g tea with 30 mL distilled water for 15 min and subsequent insertion of the TiO₂ layers for 10 min. Finally, the excess dye was rinsed with distilled water, before the front electrodes were dried in air. It should be mentioned that such natural dyes typically have a factor ~ 70 lower efficiencies than DSSCs with N719 dye [44]; however, due to our aim to work with nontoxic dyes, N719 or similar dyes are not tested here.

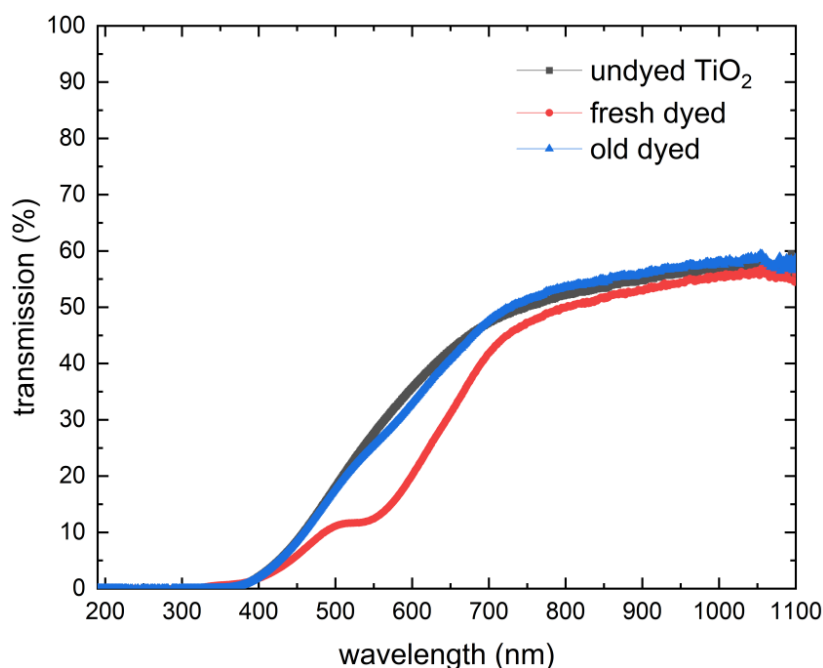


Figure 1. Transmission spectra of undyed TiO₂ on FTO coated glass, fresh and old dyed TiO₂ layers on FTO coated glass.

After preparation of front and back electrodes, the glasses were mounted with the conductive sides pointing towards each other and fixed with transparent adhesive tape. This procedure led to an efficient cell area of 6 cm², which is significantly larger than most DSSCs reported in the literature

and is well-known to reduce the efficiency [45], but improves the reliability of the measurements and was chosen as study aims at producing large-scale long-term-stable solar cells.

The glycerol electrolytes were produced by adding iodine and potassium iodide to glycerol in different concentrations (15%, 20%, and 25%) and weight-ratios (1:1, 1:1.5, 1:2, 1:2.5, and 1:3). Concentrations are given as wt% of iodine with respect to the overall mass. All prepared DSSCs are shown in Table 1. A commercial water-based iodine–triiodide electrolyte (Man Solar) was used as reference. The filling of the cells with the various electrolytes was done using capillary forces. Since this study investigates evaporation of the electrolyte, also for the possible use in textile-based solar cells, the DSSCs were not sealed.

Table 1. Samples prepared for this study.

Concentration	Ratio (w/w)	Iodine mass (g)	Potassium iodide mass (g)	Glycerol mass (g)
15%	1:1	1.50	1.50	7.00
15%	1:1.5	1.50	2.25	6.25
15%	1:2	1.50	3.00	5.50
15%	1:2.5	1.50	3.75	4.75
15%	1:3	1.50	4.50	4.00
20%	1:1	2.00	2.00	6.00
20%	1:1.5	2.00	3.00	5.00
20%	1:2	2.00	4.00	4.00
20%	1:2.5	2.00	5.00	3.00
25%	1:1	2.50	2.50	5.00
25%	1:1.5	2.50	3.75	3.75
25%	1:2	2.50	5.00	2.50

Electrical characterization was performed using a Keithley 2450 sourcemeter, illuminating the samples by a solar simulator LS0500 with AM 1.5 G spectrum (LOT-Quantum Design GmbH, Darmstadt/Germany), applying 100 mW/cm². Between measurements, the DSSCs were stored in the dark at room temperature.

3. Results and discussion

Figure 2 depicts exemplary current-voltage curves, taken on the first and on the last day of the measurements. For most curves, a change in the slope is visible, i.e. the fill factor reduces for 15%/1:2/no 3 (black curve) and 20%/1:2.5/no 1 (red curve), while the sample 25%/1:2/no 1 show a similar fill factor in both graphs. However, the curves of DSSCs with glycerol-based electrolytes have similar or even increased open-circuit voltages and short-circuit currents after more than 1 year or measurements, while the DSSC with the commercial electrolyte is clearly no longer working on the last day of the tests.

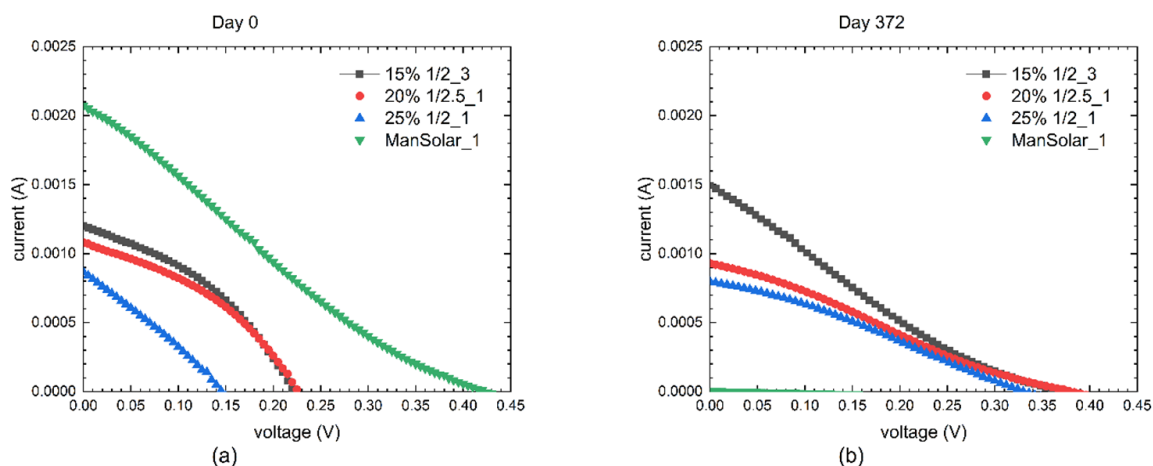


Figure 2. Current-voltage curves of exemplary DSSC with glycerol-based or commercial electrolyte: (a) measured directly after preparation (day 0); (b) measured at the end of the experiment (day 372).

Figure 3 shows the results of the long-term test of the DSSCs with commercial iodine–triiodide electrolyte. The efficiencies of the three nominally identical cells rise slightly from the first day, reaching a maximum typically around 3–5 days, and afterwards decrease significantly. After 45–90 days, the samples have nearly reached zero efficiency, clearly showing that such fluid electrolytes cannot be used in unsealed DSSCs, as it would be necessary in textile architecture.

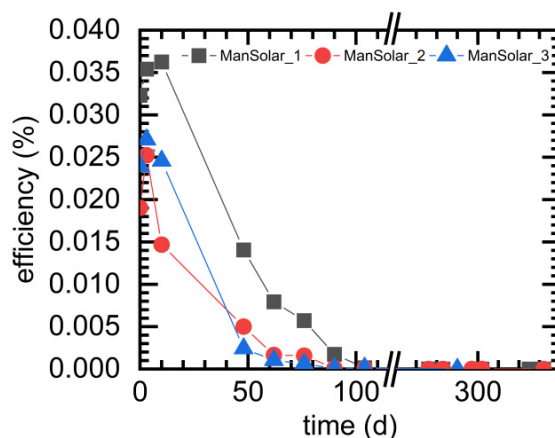


Figure 3. Efficiency of DSSCs produced with commercial fluid electrolyte, measured for approx. 1 year.

As usual for natural dyes, the energy conversion efficiencies are well below 1%, but approx. one order of magnitude higher than in cells with the previously mentioned glycerol/poly(ethylene oxide) polymer electrolytes [23]. Since this study deals with long-term stability of the electrolyte and not with improving the peak efficiency of DSSCs, the efficiency was not tried to be improved. Nevertheless, the results given here can easily be transferred to cells with toxic Ru-based dyes.

Next, the results of the long-time measurements of all samples with 15 wt% iodine are depicted in Figure 4. Here, the efficiencies during the first days are smaller than those of the commercial electrolyte, while nearly all samples maintain their original efficiency during one year of measurements. Taking into account the best specimens in each set of samples only, it can be stated that the iodine:potassium iodide mass ratio of 1:3 shows the highest efficiency. However, for most of the samples, significant deviations between the nominally identical specimens as well as between subsequent measurements are visible. These problems of imperfect reproducibility were discussed in a previous paper [23], where samples based on gel electrolytes showed even stronger irregularities.

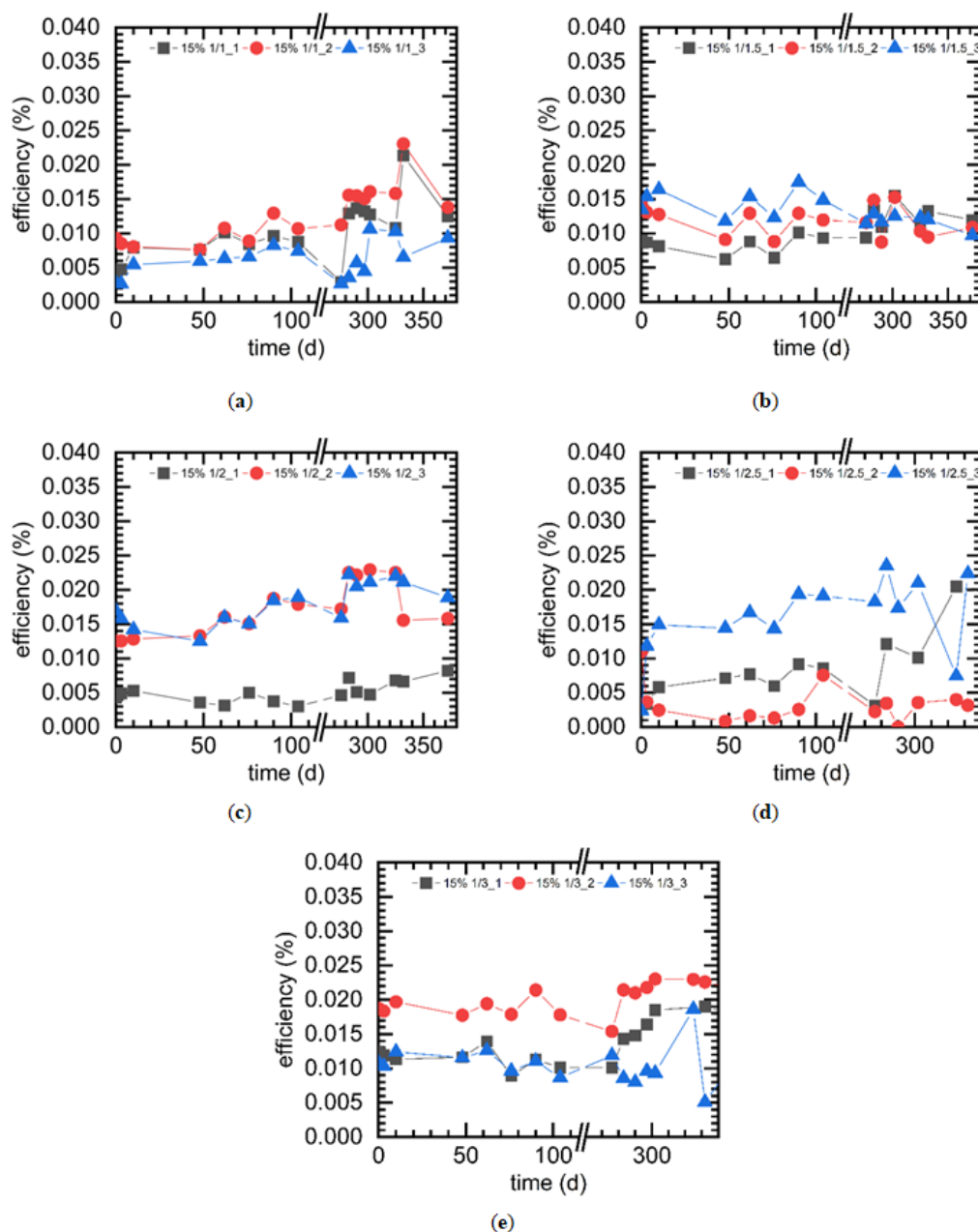


Figure 4. Efficiency of DSSCs produced with 15 wt% iodine and different iodine:potassium iodide mass ratios, measured for approx. 1 year: (a) 1:1; (b) 1:1.5; (c) 1:2; (d) 1:2.5; (e) 1:3.

On the one hand, manually preparing solar cells in the lab generally causes low reproducibility. Even with well-defined protocols regarding the application of the graphite layer, small deviations of the hand position or the pencil tip geometry will cause thicker or thinner layers and more or less FTO glass covered by graphite, leading to more or less optimized reentry efficiency of the electrons. An even more significant challenge is the thickness of the electrolyte layer which is mainly defined by the pressure between the glasses, posed by the transparent adhesive tape. Evidently, smallest deviations of the gap between both electrodes will result in significant modifications of the current in the solar cell. This explains the differences between nominally identical DSSCs during the first measurements and underlines the importance of measuring more than one specimen.

On the other hand, for later measurements, the sometimes visible severe differences between subsequent tests can be explained by the lab setup and measurement process, typically using crocodile clamps which after several measurements may destroy parts of the thin FTO layer on the glass, thus reducing the measured efficiency due to an increased contact resistance. This effect is, e.g., visible in Figure 4d in the blue line on the last-but-one day or in Figure 4e for the blue line on the last day. Such possible measurement errors also have to be taken into account during the evaluation of DSSC measurements in the lab where clamps are often used for measurements due to other problems with durable contacts.

A third point should also be mentioned. Comparing, e.g., the measurements at day 49 and the subsequent four test days, there is a certain minimum-maximum structure visible in nearly all curves. These deviations from day to day, reproduced in all cells, can typically be attributed to fluctuations in the environmental conditions, i.e. temperature and relative humidity in the lab, and indicate already the importance of taking into account such parameters, especially in case of not completely sealed DSSCs.

Next, Figure 5 shows the efficiencies of the samples prepared with 20 wt% iodine and different mass ratios of iodine:potassium iodide. While the ratio 1:1 (Figure 5a) shows firstly very low efficiencies, most specimens have more or less constant or even slightly increasing efficiencies with time. Here, the optimum ratio is 1:2.5 (Figure 5d), resulting in a highly stable efficiency over time and in the comparison of the three nominally identical specimens.

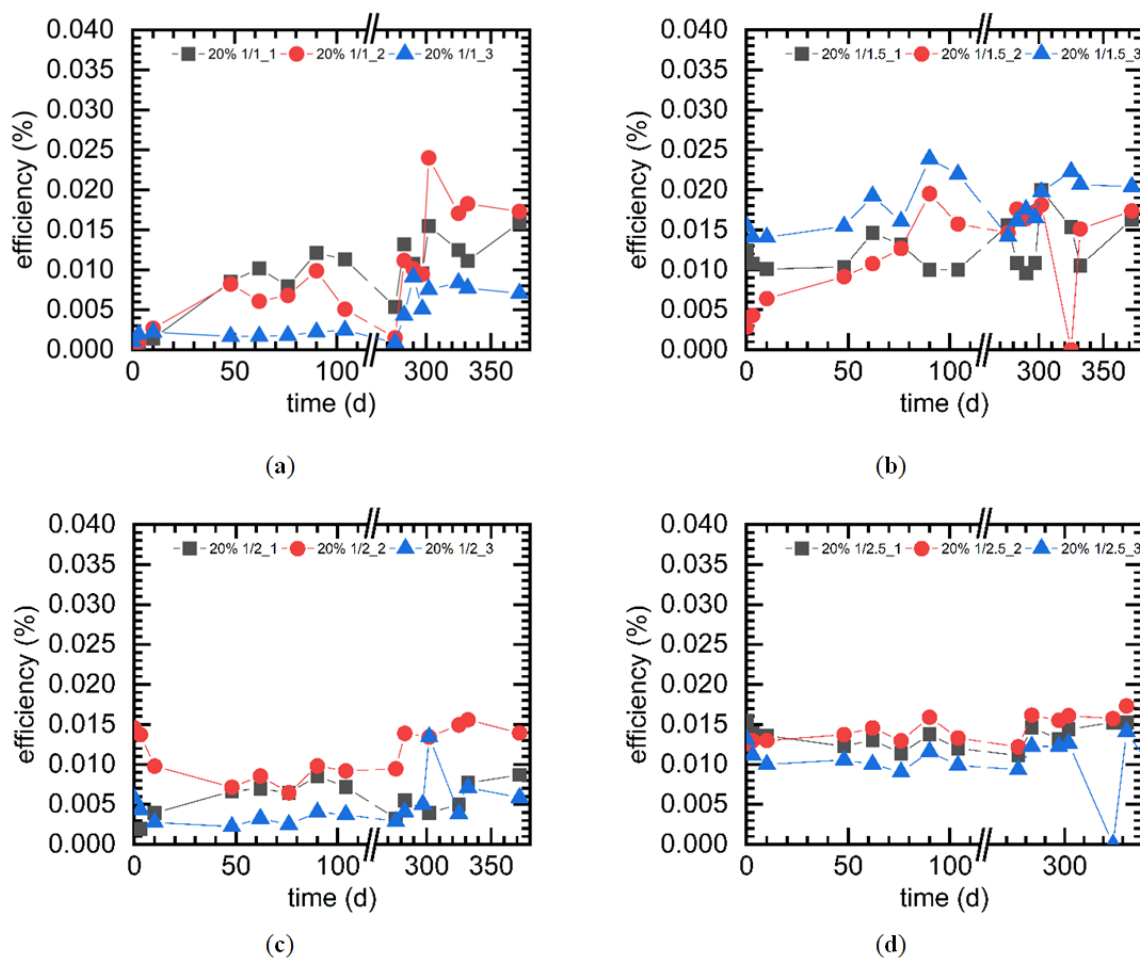


Figure 5. Efficiency of DSSCs produced with 20 wt% iodine and different iodine:potassium iodide mass ratios, measured for approx. 1 year: (a) 1:1; (b) 1:1.5; (c) 1:2; (d) 1:2.5.

Finally, Figure 6 shows the results of the long-term tests of samples with 25 wt% iodine. All samples start at very low efficiencies, especially in case of a 1:1 ratio of iodine:potassium iodide (Figure 6a). These low values during the first weeks can be attributed to the high viscosity of these samples, leading to long durations until the pores of the semiconductor are filled. Differences between the three nominally identical samples per iodine:potassium iodide mass ratio are less pronounced than for 15% iodine or for the commercial electrolyte. On the other hand, the results are less stable than for the samples with 20 wt% iodine and a 1:2.5 mass ratio of iodine:potassium iodide.

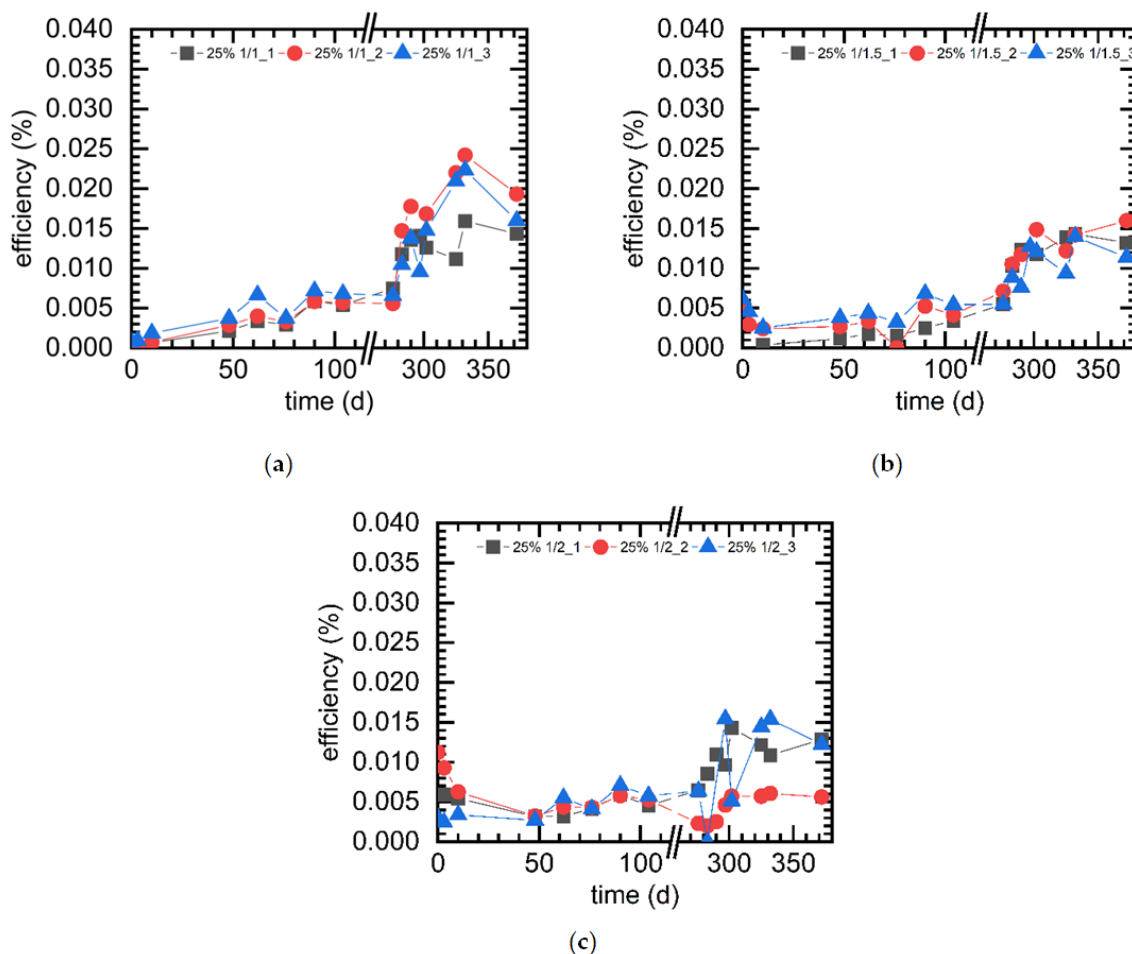


Figure 6. Efficiency of DSSCs produced with 25 wt% iodine and different iodine:potassium iodide mass ratios, measured for approx. 1 year: (a) 1:1; (b) 1:1.5; (c) 1:2.

Comparing all results, the sample with 20 wt% iodine and a 1:2.5 mass ratio of iodine:potassium iodide (Figure 5d) can be regarded as optimum, regarding reproducibility within the set of nominally identical samples and long-term stability during a year of measurements. The samples with 25 wt% iodine and the smallest amounts of potassium iodide (Figure 6a,b) show slightly higher efficiencies after one year, but significantly lower efficiencies during the first weeks, which would not make them technologically feasible.

As a next step, new specimens with 20 wt% iodine and a 1:2.5 mass ratio of iodine:potassium iodide have to be prepared to increase the efficiency by optimizing the residual parts of the solar cells, which have been used in very basic versions (e.g. without nanostructuring etc.) to enable easier comparison with results of other groups as well as to avoid undesired additional irreproducibility due to a more sophisticated design of materials and structures.

The efficiencies, open-circuit voltages and short-circuit currents are given for the first and the last day in Table 2. Here, similar trends are visible as in Figures 2 and 3—while the DSSC with commercial electrode is completely dried after more than one year, the cells with glycerol-based electrolytes are still working, in some cases better than on the first day.

Table 2. Average solar cell parameters during long-term investigation: open-circuit voltage V_{oc} , short-circuit current I_{sc} , fill factor FF and efficiency η with standard deviations.

Electrolyte	V_{oc}/V (day 0)	V_{oc}/V (day 372)	I_{sc}/mA (day 0)	I_{sc}/mA (day 372)	FF/% (day 0)	FF/% (day 372)	$\eta/\%$ (day 0)	$\eta/\%$ (day 372)
ManSolar	0.34	0.01	1.76	0	0.25 ± 0.07	-/-	0.025 ± 0.007	0.000
15%/1:1	0.16	0.26	0.58	1.13	0.34 ± 0.22	0.24 ± 0.05	0.005 ± 0.003	0.012 ± 0.002
15%/1:1.5	0.23	0.23	0.85	1.35	0.38 ± 0.08	0.21 ± 0.02	0.012 ± 0.003	0.011 ± 0.001
15%/1:2	0.21	0.24	1.12	1.17	0.29 ± 0.16	0.31 ± 0.11	0.011 ± 0.006	0.014 ± 0.005
15%/1:2.5	0.18	0.27	0.71	0.77	0.26 ± 0.22	0.41 ± 0.23	0.006 ± 0.004	0.014 ± 0.008
15%/1:3	0.21	0.36	0.94	1.33	0.43 ± 0.12	0.23 ± 0.02	0.014 ± 0.004	0.018 ± 0.002
20%/1:1	0.07	0.28	0.37	1.11	0.24 ± 0.01	0.26 ± 0.20	0.001 ± 0.000	0.013 ± 0.005
20%/1:1.5	0.18	0.30	1.06	1.51	0.32 ± 0.20	0.24 ± 0.03	0.010 ± 0.007	0.018 ± 0.002
20%/1:2	0.15	0.29	0.55	0.69	0.54 ± 0.47	0.28 ± 0.12	0.007 ± 0.006	0.009 ± 0.004
20%/1:2.5	0.22	0.38	1.02	0.85	0.37 ± 0.04	0.19 ± 0.16	0.014 ± 0.001	0.010 ± 0.008
25%/1:1	0.06	0.33	0.28	0.90	0.27 ± 0.05	0.33 ± 0.05	0.001 ± 0.000	0.017 ± 0.002
25%/1:1.5	0.16	0.34	0.69	0.72	0.30 ± 0.04	0.33 ± 0.06	0.005 ± 0.001	0.014 ± 0.002
25%/1:2	0.16	0.29	0.78	0.71	0.32 ± 0.20	0.30 ± 0.11	0.007 ± 0.004	0.010 ± 0.004

On day 0, the largest open-circuit voltages are found for the commercial ManSolar electrolyte, followed by 15%/1:1.5 and 20%/1:2.5. A clear trend, however, is not visible, which is typical for measurements during the first days when the electrolyte is not completely spread through the pores of the dyed semiconductor. On the last day of the measurements, the cells with commercial electrolyte have a voltage near zero, while all DSSCs with glycerol-based electrolytes have increased open-circuit voltages.

Comparing the short-circuit currents, the value for the cells with commercial electrolyte is again highest on day 0 and completely vanished on the last day of measurements. Most cells have increased their short-circuit currents during one year of measurements, only the cells with highly-viscous electrolytes 20%/1:2.5 and 25%/1:2 show reduced values.

Comparing the efficiencies shows again that in most cases the values for the DSSCs with glycerol-based electrolytes increase during the year of measurements, instead of reducing to zero, as the cells with the commercial electrolyte do. The fill factors decrease in most cases, but stay stable for some samples, especially those with electrolytes 25%.

These results are, to the best of our knowledge, the first values reported for a long-term study of one year. Typical long-term studies of DSSCs reported in the literature report about durations of 25–150 days [46–52], while a building-integrated (i.e. sealed) DSSC was only investigated in terms of color comfort after two years [53].

4. Conclusions

To conclude, the recent long-term study measured glycerol-based iodine-triiodide electrolytes in unsealed DSSCs with FTO glass electrodes. All DSSCs with glycerol-based electrolyte showed stable or increasing efficiencies over more than one year. By modifying the iodine-triiodide ratio, specimens with 20 wt% iodine and a 1:2.5 mass ratio of iodine:potassium iodide were found to have the highest efficiency along the whole measuring duration, with larger amounts of iodine being potentially interesting if a method can be developed to reach the maximum efficiencies earlier.

Next tests will concentrate on developing DSSCs with this electrolyte further to improve the overall efficiency while maintaining the long-term stability enabled by this novel electrolyte.

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Conflict of interest

The authors declare no conflict of interest.

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