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Author(s): Miettunen, Kati & Ruan, Xiaoli & Saukkonen, Tapio & Halme, Janne & Toivola, Minna & Guangsheng, Huang & Lund, Peter

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Stability of Dye Solar Cells with Photoelectrode on Metal Substrates

Kati Miettunen^{,a}, Xiaoli Ruan^b, Tapio Saukkonen^c, Janne Halme^a, Minna Toivola^a, Huang
Guangsheng^b, Peter Lund^a*

^{a)} New Energy Technologies Group, Department of Applied Physics, Helsinki University of
Technology, P.O. BOX 5100, FIN-02015 TKK, Finland

^{b)} College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China

^{c)} Engineering Materials Group, Department of Engineering Design and Production, Helsinki University
of Technology, P.O. BOX 4200, FIN-02015 TKK, Finland

Abstract

In this study the stability of dye solar cells with different kinds of metals as the photoelectrode substrate is studied. Stainless steels, Inconel and titanium substrates were tested in order to find stable substrate options. Photovoltaic characterization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and substrate polarization measurements were used in the characterization. Dye solar cells based on different grades of stainless steel suffered from rapid degradation of efficiency within few hours in light soaking. Good stability was demonstrated with dye solar cells with Inconel and Ti photoelectrode substrates. The Inconel substrates have thick passive oxide layer which is likely related to the good stability. However according to EIS analysis, the oxide layer of Inconel substrates increased resistive losses which caused lower fill factor and photovoltaic efficiency compared to Ti based cells.

Keywords: dye-sensitized, aging, impedance spectroscopy

1. Introduction

Nanostructured dye solar cells (DSC) are easy to manufacture and they can be prepared from cheap materials. An important step in the commercialization of these cells would be the use of flexible substrates instead of conventional rigid glass substrates so that roll-to-roll mass production methods could be employed. Using a thin metal sheet as an electrode substrate is appealing since in addition to flexibility they have superior conductivity compared to transparent conducting oxide (TCO) layers used on glass and plastic substrates. Furthermore, some metal substrates endure high temperature treatments which are needed in the preparation of high quality photoelectrodes. In fact the highest efficiency of flexible DSC reported, 8.6 %, was obtained with a solar cell with the photoelectrode on metal.¹ This is even though there are additional optical losses in the cell configuration, in which metals are used as a photoelectrode substrate, since the light has to penetrate both the counter electrode and the electrolyte layer.

The problem with many metals is that they corrode in the iodine containing electrolyte.²⁻⁴ The cheapest metal that has met the basic stability requirement i.e. survived electrolyte soaking tests is stainless steel (StS) 304.²⁻⁴ However in our recent study,⁵ we noted that there are significant stability problems when StS 304 is used as a photoelectrode substrate in complete dye solar cells: under 1 Sun illumination the cells lost about 80 % of its efficiency within few hours. The degradation was either significantly accelerated or triggered by working conditions (i.e. under illumination).⁵ Interestingly enough, there were signs of neither corrosion nor contamination.^{5,6} In the tests, we tried for instance to contaminate a glass based photoelectrode with StS, but no metal contamination could be seen as there was no affect to the cell performance.⁶ In addition, it was discovered that the electrolyte in these cells is

not apparently subject to significant changes during the degradation.⁵ Thus the origin of the instability of StS 304 based photoelectrodes is still unknown.

The purpose of this study is to determine what kind of metal would be sufficiently stable to be used as such as the photoelectrode substrate. Using inherently stable materials rather than protective coatings is attractive since less processing steps are required in the manufacturing of the cells. The studied materials are different grades of stainless steel, Inconel and titanium. Electrochemical characterization of the dye solar cell with metal substrates is carried out to understand the differences in the photovoltaic performance of the cells.

2. Experimental Methods

2.1. Samples. The studied metal substrates were stainless steel 304 (1.25 mm, Outokumpu Ltd.), 321 (0.05 mm, Goodfellow), 316 (1.25 mm, Outokumpu Ltd.), 316L (0.05 mm, Goodfellow), Inconel alloy 600 (0.075 mm, Goodfellow), and 2 titanium foils (thicknesses 0.03 mm and 0.13 mm, referred later in the text by their thickness). The main elemental components of the different metals are listed in Table 1. The main difference among the different stainless steel types is the use of additives such as Mo and Ti. The difference between Inconel and StS types is the proportion of Fe and Ni: while Inconel is mainly composed of Ni and has some Fe, StS is mainly of Fe and has some Ni (Table 1). The other electrodes and reference glass cells are prepared on fluorine-doped tin oxide (FTO) coated glass (3 mm, Pilkington TEC-8, sheet resistance 8 Ω /sq, Hartford Glass Company, Inc.). Before use the substrates were washed with mild detergent and rinsed in tap water followed by three minutes in an ultrasonic bath first in ethanol and then in acetone.

Porous TiO₂ layers were prepared by doctor blading using a commercial titania paste (Dyesol, DSL 18NR-T). The resulting TiO₂ layer thickness was measured to be about 15 μ m using a Dektak 6M stylus profiler (Veeco Instruments), except for the layers on Ti 0.03 substrate; in which case as the metal foil was very thin, it bended in the deposition so that there was less paste in the middle of the film. In general we noticed that metal films with thickness approximately 0.05 mm were the easiest to handle in

the different phases of the processing. The photoelectrodes were sintered at 450 °C for 30 minutes in Lenton EF 11/8B furnace. The treatment included also 10 minutes heating up ramp from room temperature to 450 °C and 30 minutes cooling down to 70 °C. After the heat treatment they were placed for 16 h in a dye solution consisting of 0.32 mM *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (Dyesol, N-719) in ethanol (99.5 wt-%).

The counter electrodes were prepared on FTO glass substrates with the thermal platinization method⁷ using 10 mM tetrachloroplatinate PtCl₄ (Sigma-Aldrich) dissolved in 2-propanol. The counter electrodes were thermally treated at 385 °C for 15 min.

25 μm thick Surlyn 1702 ionomer resin film (DuPont) was used as spacer. Electrolyte consisting of 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile was inserted through filling channels on the glass substrate which were then closed with a 40 μm thick Surlyn 1601 foil (DuPont) and a thin cover glass. In the long term aging tests, we used HSE-EL liquid electrolyte by Dyesol. Before use, the foils were washed with similar ultrasonic baths as the substrates. Copper tapes were employed as current collector contacts and Electrolube conductive silver paint was applied on the edge of the conductive tape and the substrate to reduce resistance. The structure of the cells was not optimized for high performance.

In addition to the complete solar cells, substrate - counter electrode (SU-CE) cells⁸ were prepared to study current leakage from the different substrates. The substrates were thermally treated and dyed the same way as the actual photoelectrodes since both of these treatments affect their electrochemical properties.^{9,10}

2.2. Measurements. Photovoltaic measurements were performed using a solar simulator with halogen lamps (Philips projection lamp, type 13117) providing 1000 W/m² AM1.5G (1 Sun) equivalent light intensity at 25 °C determined by a calibrated silicon reference cell with spectral filter to mimic typical DSC response. The IV curves were measured using a Keithley 2420 SourceMeter. The solar cells were

provided with black masks since using a mask with a slightly larger aperture size compared to the active area of the cell leads to the most reliable results according to the literature.¹¹

The light soaking system was also composed of halogen lamps providing conditions approximately equivalent to 1 Sun at ~40 °C temperature. The open-circuit voltage V_{OC} and short circuit current density i_{sc} were recorded with an Agilent 34980A datalogger in 15 minutes intervals. The cells were kept in open circuit conditions between the measurements. Complete IV curves were measured once a week using an Autolab PGSTAT302N electrochemical test station.

Steady state IV measurements of the SU-CE cells were performed also with the Autolab PGSTAT302N electrochemical test station. To avoid hysteresis, the IV curves in the voltage range -1 – 1 V were measured in 20 mV intervals with 20 s stabilization time for each voltage point.

Electrochemical impedance spectroscopy (EIS) was performed over the frequency range 100 mHz – 100 kHz with Zahner Elektrik's IM6 Impedance Measurement unit. The EIS measurements were taken in the dark in voltage range 0 - -0.7 V using 10 mV amplitude. Frequency range 100 mHz - 100 kHz was measured twice to analyze the stability of the measurement. ZView2 software was employed in the equivalent circuit analysis.

The surface morphology and elemental composition analysis of the substrates of the aged cells were examined with a Zeiss Ultra 55 field emission scanning electron microscope (SEM) equipped with a Bruker AXS energy dispersive x-ray spectroscopy (EDS) equipment controlled with Quantax 400 software. The electrolyte of the aged cells was examined with Nicolet 380 FT-IR Spectrometer using KBr tablets.

3. Results and Discussion

3.1. Initial Photovoltaic Performance. The cells with metal photoelectrode show lower short-circuit current i_{sc} than FTO based cells (Table 2). This is mainly because the counter electrode and the bulk electrolyte are shading the photoelectrode in the metal cells. In addition due to the reversed light direction, electrons are generated on average further away from the photoelectrode substrate which may

decrease the collection efficiency. The losses resulted in by the reverse illumination listed above can be approximated by comparing FTO glass based cells measured in normal way and with reverse side (Table 2) and it can be seen that reverse illumination indeed is responsible for most of the difference between normally measured glass cells and metal based cells. Multiple and back reflection of light within the cell differ between metal and glass substrates which poses uncertainty to the comparison of the i_{sc} values so that the analysis is merely qualitative.

Among the metal based cells, the highest i_{sc} values were gained with Ti 0.13 metal foil and Inconel whereas the lowest one with StS 316L and StS 321 cells (Table 2). The smaller i_{sc} of Ti 0.03 compared to Ti 0.13 was due to a thinner TiO_2 layer which was caused by problems in the deposition of the film described in the experimental section. Interestingly, the difference with the highest and the lowest i_{sc} is more than 40 % among the different metals causing a large difference also in cell efficiencies (Table 2). The metal substrates do have a mirror effect and the reflectance of the substrate may differ causing some difference in the i_{sc} values. However, the difference in i_{sc} is so large that according to our calculations it cannot be explained with such an optical effect. If current leakage from the substrate to the electrolyte is significant that may affect V_{oc} , but it should have only a minor effect on i_{sc} .¹² Hence, the large differences in i_{sc} and η are not likely caused by current leakage via substrate. As the degradation of the StS (304) PE cells is very rapid and affects primarily i_{sc} and secondarily V_{oc} ,⁵ it might be that the cells with low i_{sc} are already in the initial measurements affected by the degradation. This hypothesis is analyzed more in section 3.2.

There is some 50 mV difference also in the open-circuit voltage among the metal based cells (Table 2). The highest V_{oc} with the metal DSCs was with Ti and Inconel, which maybe related to either small current leakage from the substrate or better stability. These features are discussed more later on.

There are clear differences also in the fill factor FF (Table 2): The highest FF , about 70 %, is reached when using Ti 0.13 substrate. StS 304, StS 316, StS 321 and FTO cells have FF approximately 63 %. Interestingly, with Inconel FF is only 56 %. Fill factor is affected by the charge transfer resistance at the counter electrode, diffusion in the electrolyte, charge transport and transfer resistances in the TiO_2 film,

sheet resistance of the substrates, and charge transfer resistance between the TiO₂ and the photoelectrode substrate.¹³ The four first mentioned should be similar due to the similar materials and methods used in the manufacturing. The latter two ones are related to the photoelectrode substrate. The possibility that the sheet resistance of the substrate could cause differences between these metals cell can, however, be omitted since all the metals have superior conductivity compared to the other cell components. Hence, the differences in the very minor loss mechanisms lead to negligible effect on the IV curve. On the other hand, the effect of charge transfer resistance between the PE substrate and the TiO₂ layer is a likely cause and it is examined with impedance spectroscopy in section 3.6.

3.2. Aging of the cells. The solar cells were aged under 1 Sun illumination at 40 °C. All the studied stainless steel cell types degraded within few hours (Figure 1a). The almost complete loss of i_{sc} and the following loss in the efficiency were the main factors in the aging of the StS based cells, which were shown for StS 304 already in our previous publication.⁵ The loss of V_{oc} was not that detrimental in the StS based cells (Figure 1b). Our previous study showed already that there were not, however, changes in the fill factor in the aging of the StS 304 type cells.⁵ Interestingly, the cells with StS metals 316 and 316L, which are less prone to corrosion than StS 304, showed slightly faster degradation. This suggests that the reason for the degradation of the DSCs with StS photoelectrodes is not corrosion. This view is supported also by our previous studies in which neither visual inspection nor SEM and EDS analyses revealed any marks of corrosion of StS 304 when used as photoelectrode substrate.⁵ Here in accordance, SEM and EDS analyses did not reveal any changes in the other metal substrates either. As an example Figure 2 shows the SEM data of StS 316L substrate, which shows that only the initial grain boundaries and some other features that relate to the manufacturing of the metal but no change due to aging. For instance general corrosion should leave marks, basically pit holes, that are clearly visible in SEM,¹⁴ but here such were not detected. The electrolyte of the aged cells was analyzed with FT-IR. The electrolyte of an aged StS 304 cells had similar spectra in the studied range 400-4000 cm⁻¹ as that of a FTO cell

implying there were no significant changes in the electrolyte that could be related to the aging of the StS cells.

The most rapid degradation (under 15 minutes) was seen in the case of StS 321 cells (Figure 2a) which had also the poorest initial efficiency (Table 2). As the degradation of the StS based cell was very fast, it is likely that those had degraded even before the initial measurements, which would explain the differences in particular in the i_{sc} values compared to Inconel and Ti 0.03 cells. The Ti 0.13 cells suffered from leakage of the electrolyte and thus their aging performance is not discussed more in this section. The leakage occurred because Ti 0.13 foil was received as a roll and it due to its thickness did not straighten flat enough which resulted in problems in the sealing.

The Ti 0.03, Inconel and reference FTO cells were stable in the 1 day short-term testing (Figure 1) but also during the long term test of one month (Figure 3). It is typical for i_{sc} to slightly decrease and for V_{oc} to increase in the beginning when the cells are still stabilizing after preparation (Figures 1 and 3), typically causing even increase in the efficiency (Figure 3d). The initial performance of the cells in Table 2 and Figure 3 has some difference due to the different composition in the electrolyte. We and also others have in fact expected Ti based cells to be stable.¹⁵ This is because the Ti metal foil is covered naturally with oxidized titanium and titanium oxides such as TiO_2 have proven to be a stable option for the porous photoelectrode.

3.3. Current leakage via substrate. Leakage current from the different substrates to the electrolyte is represented in Figure 4, in which negative voltages represent the normal operating voltages. The substrates were thermally treated and dyed in order to mimic the effect of the photoelectrode substrate in complete cells. The FTO substrates had the highest leakage current and the different StS types had a slightly smaller compared to FTO (Figure 4). The smallest leakage current was from the Ti substrates, which was to be expected since titanium oxide layers are commonly used as blocking layers to prevent current leakage^{8,9,16} and Ti substrates are inherently covered with Ti oxides. Interestingly, the largest difference between the Ti substrates and the other studied substrates is in the reverse bias, i.e. positive

voltages (Figure 4). The substrate mediated current leakage typically affects V_{OC} ,⁹ and indeed high V_{OC} values were measured with Ti and Inconel (Table 2) which had the smallest leakage current (Figure 4). According to the literature, the small leakage current from these substrates should play even more important role at low light intensities.^{8,9,17} The differences in the photovoltaic performance between different StS types (Table 2) are not linked to current leakage from the substrate since the $i-V$ curves of the substrates was in practice similar (Figure 4).

3.4. Electrochemical Impedance Spectroscopy. A commonly used equivalent circuit model^{8,13,18,19} (Figure 5) was used in the fitting of the EIS data, example data are presented in Figure 6. The complete dye solar cell equivalent circuit model is dominated by different components at different voltages.^{6,8,18} In this publication we use the same circuits that we employed in our previous publication.⁸ In the circuit, constant phase elements (CPE) are and their impedance of a constant phase element Z_{CPE} is determined by the pre-factor Q and the exponent β as follows:

$$Z_{CPE} = \frac{1}{Q(j\omega)^\beta} \quad (1)$$

where ω is the angular frequency and j is the imaginary unit. Factor β takes into account the porosity and unevenness of a realistic electrode surface which results in dispersion in the related R and C values. The dispersion of the values shows as flattening of the semi-circle in Nyquist plots such as in Figure 6a.

In the voltage range 0 – -0.4 V, the charge transfer resistance either at the substrate/electrolyte interface R_{SU} or at the TiO_2 /electrolyte interface R_{CT} is governing the response and only one semi-circle can be detected. From -0.5 V to -0.7 V, two separate semicircles was seen (Figure 6a): the one at lower frequencies relates to photoelectrode and the one at high frequencies typically represents the counter electrode. However, occasionally at the high frequencies the effect of the charge transfer resistance between the TiO_2 layer and the photoelectrode substrate R_{CO} is overlapping charge transfer resistance at

the counter electrode R_{CE} .^{8,20} Indeed, such an effect could also be seen here in the case of Inconel PE substrate as discussed in detail in section 3.6.

3.5. The photoelectrode charge transfer resistance in the initial state.

R_{LF} and C_{LF} mark for the EIS component detected in low frequencies, which depending on the voltage, is caused mainly either by $R_{SU} - CPE_{SU}$ or by $R_{CT} - CPE_{CT}$ pair (Figure 5).^{8,18} The largest recombination resistance was obtained with Ti substrates (Figure 7a). This was to be expected since the effect of the substrate dominates in the small negative voltages (smaller than -0.4 V)^{12,18} and Ti substrates had smallest current leakage in the substrate analysis (Figure 4). As noted also before for StS 304 compared to FTO,^{5,6} the DSCs with StS PE have lower recombination resistance compared to Ti, Inconel, and FTO glass (Figure 7a) even though the current leakage from the substrate was measured to be smaller or the same as from glass substrates (Figure 4). Hence, it might be that the small initial value R_{LF} of differences of R_{LF} and C_{LF} (Figure 7) in the StS based cells are already in the initial state are arising from the instability rather than from steady characteristic as the degradation is very rapid. In our previous study, we noted that the R_{LF} of cells with StS 304 PE decreases over time,⁵ which supports the idea that instability may have affected the performance already in the initial state.

3.6. Charge transfer resistance at the high frequency in initial state.

In this section, we study the semi-circle at the high frequency (Figure 6). In our previous publication we did not detect any changes in R_{CE} of StS 304 based cells and furthermore changes in R_{CE} would not anyway explain the degradation seen in the case of StS based cells as the primarily effect would not be on i_{SC} but on FF .⁵ Thus the focus of this section is in understanding the performance differences in the initial state. Namely, the main issue is to determine whether it is caused solely by R_{CE} or also by R_{CO} . In the analysis, we use the same approach as in our previous publication.⁸ The method is based on the fact that quantitative analysis of the electrodes can be reached by analyzing the data as a function of external

current.^{6,8} Using this easy approach, we avoid application of reference electrodes into the cells which is challenging as the cells are only 20 μm thick.

The width of the semi-circle at the high frequencies R_{HF} for different cell types is shown in Figure 8. Most of the cells gave similar R_{HF} . The glass cells are similar to those used in our previous study⁸ where it was confirmed that the response was caused by R_{CE} . Hence, for most of cells R_{HF} can be attributed to R_{CE} since there is not significant deviation from the R_{HF} values of the glass cells.

The cells with Inconel PE substrate make an exception to this trend as R_{HF} in their case was much higher than in the other cells showing only R_{CE} . The deviation of the R_{HF} from R_{CE} is apparently caused by R_{CO} in Inconel cells. This is because the cells were similar apart from the photoelectrode substrate and the dependence of R_{HF} on the substrate suggests that it is linked to an interfacial resistance of the substrate leaving R_{CO} as the suiting component. Similar effect has been detected with other substrates also previously.^{8,20} In addition, the semi-circle corresponding to R_{HF} in Inconel cells was quite flat (Figure 6a) with the factor β being 0.65 – 0.7 which suits well for the case of two semi-circles overlapping each other but having slight difference in the related time constants. In the other high frequency semicircles β was ~ 0.9 which is typical for a single interface.

The oxide layers covering the different metals are different which may cause the difference in the resistance between the PE substrate and the TiO_2 layer. Inconel metals have particularly thick passivating oxide layers, which could explain why there would have been significant R_{CO} . The presence of significant R_{CO} is the most likely cause for the low fill factor (Table 2) of the Inconel based cells.

4. Conclusions

The aim of this study was to examine the stability of different metals as photoelectrode substrates in dye solar cells. It was detected that all the cells with photoelectrodes deposited on different types of stainless steels degraded in a matter of hours under illumination. On the contrary, Inconel and titanium based DSCs demonstrated good stability in the 1 month long light soaking test.

The mechanisms of the rapid degradation of stainless steel based DSCs remained still unclear. Further confirmation was, however, found that the stainless steel photoelectrodes do not according to SEM and FT-IR analyses suffer from corrosion. This point was even further clarified as the use of stainless steel qualities which are less prone to corrosion did not slow down the aging. The stability of Ti substrates was expected as Ti metal is covered with titanium oxide layer (cf. TiO₂ photoelectrodes are stable). Inconel metal on the other hand is covered with thick passivating oxide layer which is likely related to its good stability.

In the case of Inconel there were additional resistances detected in EIS analysis lowering the fill factor which were apparently caused by the protective passive layer. This is because the resistance was caused by an interfacial resistance between the TiO₂ layer and the substrate. With Ti foils such resistances were not detected and furthermore they have low leakage current which is an important feature especially in low light intensity conditions. However, the problem with both titanium and Inconel is their high cost. Therefore, it might be beneficial to coat some cheaper metal with these more stable metals.

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References

- [1] H. Park, Y. Jun, H.-G. Yun, S.-Y. Lee, M.G. Kang, *J. Electrochem. Soc.* 155 (2008) F145-F149.
- [2] M. Toivola, F. Ahlskog, P. Lund, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2881-2893.
- [3] T. Ma, X. Fang, M. Akiyama, K. Inoue, H. Noma, E. Abe, *J. Electroanal. Chem.* 574 (2004) 77-83.
- [4] X. Fang, T. Ma, M. Akiyama, G. Guan, S. Tsunematsu, E. Abe, *Thin Solid Films* 472 (2005) 242-245.
- [5] K. Miettunen, J. Halme, P. Lund, *J. Phys. Chem. C* 113 (2009) 10297-10302.
- [6] K. Miettunen, J. Halme, M. Toivola, P. Lund, *J. Phys. Chem. C* 112 (2008) 4011-4017.
- [7] N. Papageorgiou, W.F. Maier, M. Grätzel, *J. Electrochem. Soc.* 144 (1997) 876-884.
- [8] K. Miettunen, J. Halme, P. Vahermaa, T. Saukkonen, M. Toivola, P. Lund, *J. Electrochem. Soc.* 156 (2009) B876-B883.
- [9] P.J. Cameron, L.M. Peter, S. Hore, *J. Phys. Chem. B* 109 (2005) 930-936.
- [10] R. Sastrawan, J. Renz, C. Prah, J. Beier, A. Hinsch, R. Kern, *J. Photochem. Photobiol. A - Chem.* 178 (2006) 33-40.
- [11] S. Ito, K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. Zakeeruddin, M. Grätzel, *Prog. Photovolt: Res. Appl.* 14 (2006) 581-601.
- [12] P.J. Cameron, L.M. Peter, *J. Phys. Chem. B* 109 (2005) 7392-7398.
- [13] F. Fabregat-Santiago, J. Bisquert, E. Palomares, L. Otero, D. Kuang, S.M. Zakeeruddin, M. Grätzel, *J. Phys. Chem. C* 111 (2007) 6550-6560.

- [14] K. Miettunen, D.Sc. Thesis, Helsinki University of Technology, Finland, 2009.
- [15] S. Ito, N.-L. C. Ha, G. Rothenberger, P. Liska, P. Comte, S. M. Zakeeruddin, P. Pechy, M. K. Nazeeruddin, M. Grätzel, *Chem. Commun.* 38 (2006) 4004-4006.
- [16] J. Xia, N. Masaki, K. Jiang, S. Yanagida, *J. Phys. Chem. B* 110 (2006) 25222-25228.
- [17] S. Hore, R. Kern, *Appl. Phys. Lett.* 87 (2005) 263504.
- [18] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, A. Hagfeldt, *Sol. Energy Mater. Sol. Cells* 87 (2005) 117-131.
- [19] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, N. S. Ferriols, P. Bogdanoff, E.C. Pereira, *J. Phys Chem. B*, 104 (2000) 2287-2298.
- [20] T. Hoshikawa, M. Yamada, R. Kikuchi, K. Eguchi, *J. Electrochem. Soc.* 152 (2005) E68-E73.

Table 1. The chemical composition (%) of different stainless steel types and Inconel 600 according to the data supplied by the manufacturer.

	Fe	Cr	Ni	Mo	Co	Others
StS 304	balance	18.1	8.1			C
StS 316	balance	17.2	10.1	2.1		C
StS 316L	balance	18	10	3		C
StS 321	balance	18	9			Ti, C
Inconel	8	16	72		balance	Mn, Si, C, S

Table 2. Average initial performance characteristics of the cells with different photoelectrode substrates and their standard deviations. The glass cells were measured also with reverse illumination.

substrate	number of cells	i_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
Glass	5	11.3 ± 0.3	-637 ± 6	63 ± 1	4.6 ± 0.1
Glass – reverse	5	8.7 ± 0.5	-609 ± 4	67 ± 1	3.5 ± 0.1
StS 304	5	7.2 ± 0.4	-611 ± 7	64 ± 1	2.8 ± 0.2
StS 316	4	6.5 ± 0.6	-610 ± 10	63 ± 1	2.5 ± 0.3
StS 316L	4	4.6 ± 0.3	-571 ± 3	58 ± 1	1.5 ± 0.1
StS 321	3	4.7 ± 0.9	-580 ± 30	63 ± 1	1.7 ± 0.4
Inconel	4	8.0 ± 0.2	-630 ± 15	56 ± 2	2.8 ± 0.1
Ti 0.03	3	7.0 ± 1.1	-630 ± 17	68 ± 3	3.0 ± 0.4
Ti 0.13	3	7.9 ± 0.8	-620 ± 12	70 ± 1	3.4 ± 0.4

Figure captions:

Figure 1. Typical a) i_{sc} and b) V_{OC} in different metal cells over the first 24 h of light soaking in 1 sun. The values are measured in 15 minutes interval. In b, the V_{OC} values of Ti, Inconel and glass cell data are overlapping.

Figure 2. Example SEM data of a) a StS 316L substrate before the cell assembly and b) a 316L substrate from an aged DSC.

Figure 3. Typical a) i_{sc} , b) V_{OC} c) FF and η data of Inconel (green box), Ti 0.03 (orange triangle) and glass (black cross) over 4 weeks of light soaking in 1 sun. These cells were filled with HSE-EL electrolyte.

Figure 4. i - V curves of different high temperature treated and dyed substrates. The data is the average i - V curve of three samples. The curves of glass and different StS types are overlapping.

Figure 5. Equivalent circuit model of a DSC:⁸ R_s is the ohmic series resistance caused by sheet resistance of the substrates, current collector contacts etc. CPE_{SU} and R_{SU} are the CPE and charge transfer resistance at the PE substrate/electrolyte interface. CPE_{CO} and R_{CO} are the CPE and charge transfer resistance between the PE substrate and the porous TiO_2 . $R_t (= r_t d)$ is the electron transport resistance and d is the thickness of the layer. $CPE_{CT} (= cpe_{CT}/d)$ and $R_{CT} (= r_{CT}/d)$ are the CPE and the charge transfer resistance at the TiO_2 /electrolyte interface. Z_d is the mass transfer impedance at the counter electrode due to ionic diffusion in the electrolyte. CPE_{CE} and R_{CE} are the CPE and charge transfer resistance at the counter electrode/electrolyte interface.

Figure 6. Example EIS data of StS 304, Inconel, and glass based DSCs at -0.6 V in dark. The data is presented as a) a Nyquist plot and b) imaginary impedance Z'' vs. frequency f . The markers refer to measured data and the continuous lines to fitted data.

Figure 7. Initial a) R_{LF} and b) C_{LF} of the typical metal cells as a function of cell voltage. In the case of some cells, only the upper limit of R_{LF} could be determined at the voltages more negative than -0.5 – -0.6 V due to the Gerischer type response.⁸

Figure 8. Initial R_{HF} in the different kinds of DSCs. The data of one cell type combines data from multiple cells. One of the trend lines represents Inconel cells whereas the other trend line attributes to all the other studied cells.

Figure 1.

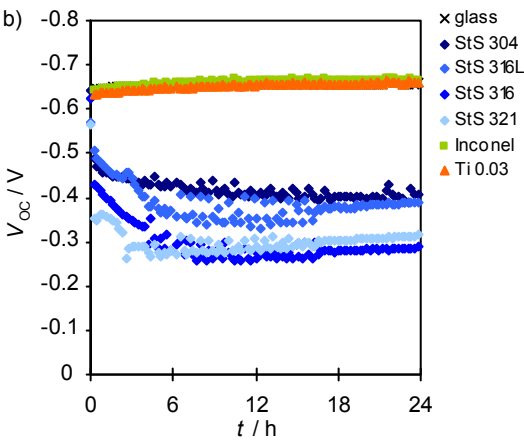
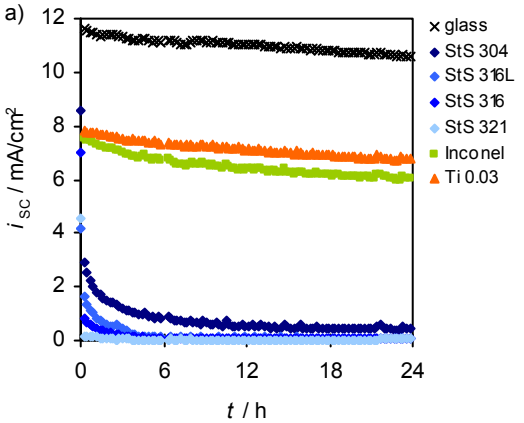


Figure 2.

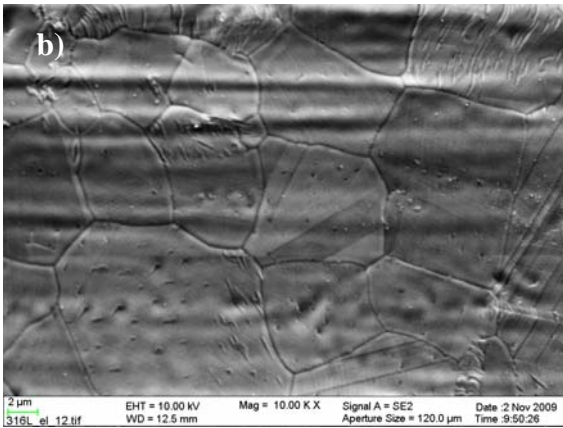
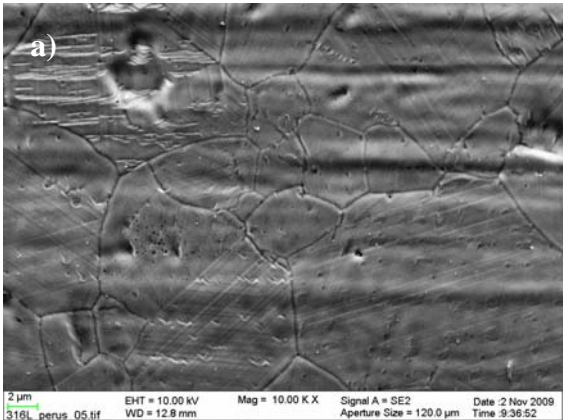


Figure 3.

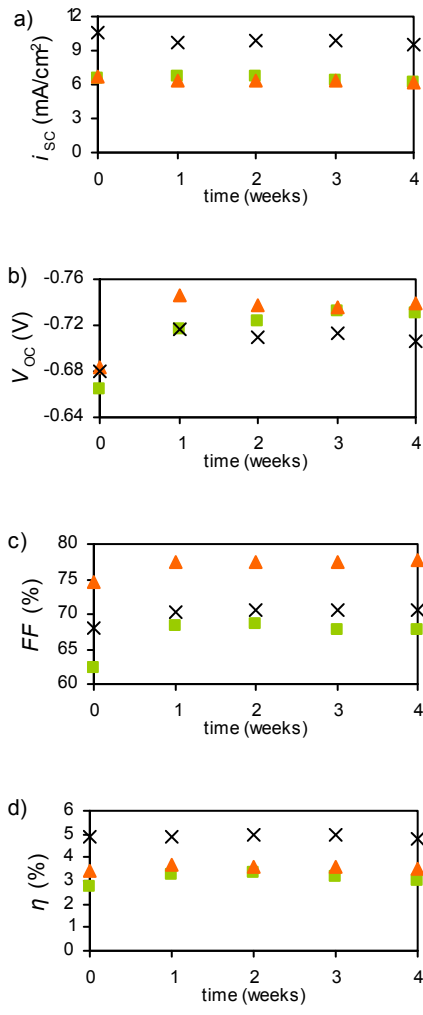


Figure 4.

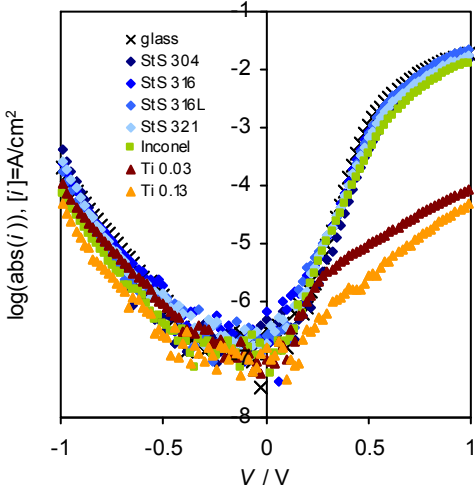


Figure 5.

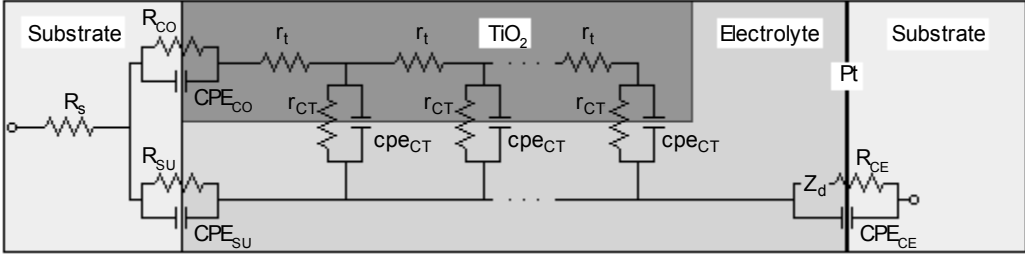


Figure 6.

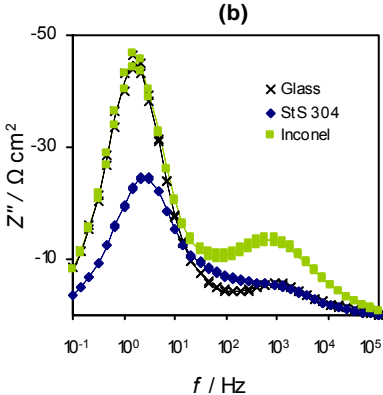
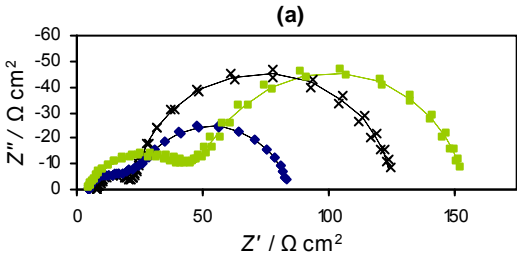


Figure 7.

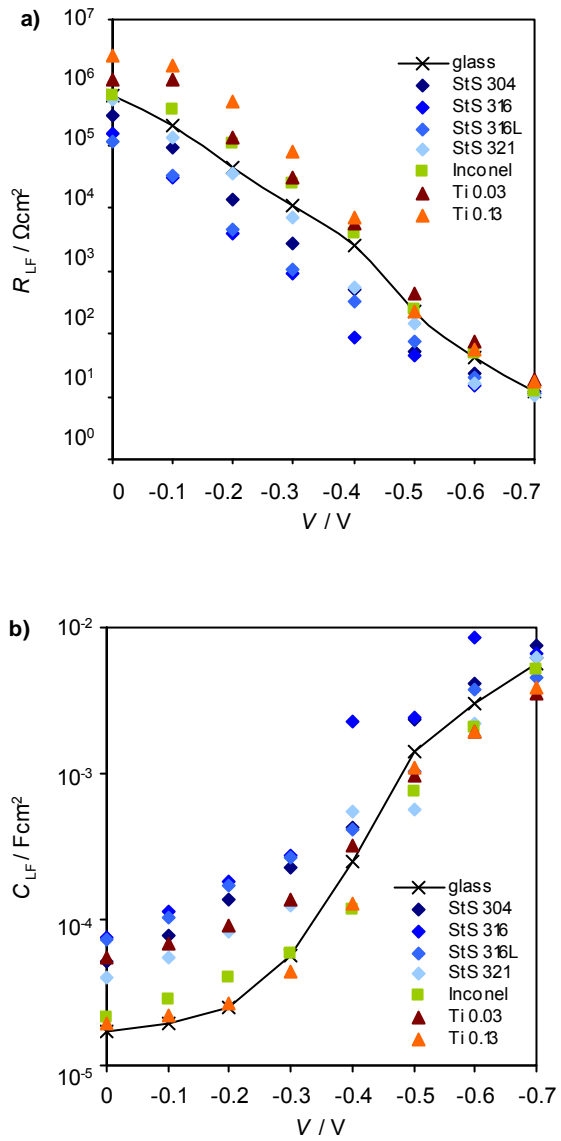


Figure 8.

