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Author(s): Miettunen, Kati & Jouttijärvi, Sami & Jiang, Roger & Saukkonen, Tapio & Romu, Jyrki & Halme, Janne & Lund, Peter

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Low cost ferritic stainless steel in dye sensitized solar cells with cobalt complex electrolyte

Kati Miettunen^{,a}, Sami Jouttijärvi^a, Roger Jiang^b, Tapio Saukkonen^c, Jyrki Romu^c,
Janne Halme^a, Peter Lund^a*

^a Aalto University, New Energy Technologies Group, Department of Applied Physics,
P.O. BOX 15100, FIN-00076 Aalto, Finland

^b Imperial College London, Department of Chemistry, London SW7 2AZ, UK

^c Aalto University, Engineering Materials Group, Department of Engineering Design and
Production, P.O. BOX 14200, FIN-00076 Aalto, Finland

* Corresponding author: Telephone: +358 50 3441729.

E-mail address: kati.miettunen@aalto.fi.

Abstract

Cheap ferritic stainless steel is applied here as the counter electrode substrate in dye sensitized solar cells with cobalt complex electrolyte. A 5.0 % efficiency was reached with these type of cells which is more than 2.5 times higher compared to previously reported devices with metal counter electrode and cobalt complex electrolyte. The electrochemical impedance spectra analysis showed that the best cells with the ferritic steel counter electrode had as low charge transfer resistance ($3.6 \Omega\text{cm}^2$) as the reference glass cells with the same electrolyte. While in previous studies many metals have corroded in the cobalt complex electrolyte, the stability analysis including scanning electron microscope imaging of the aged electrodes suggested that the ferritic stainless steel substrates did not corrode in the electrolyte. Hence ferritic stainless steel appears as a possible alternative counter electrode in dye solar cells with cobalt electrolyte in terms of cost, performance and stability.

Keywords: Metals; Stability; Redox couple, Corrosion

1. Introduction

Dye sensitized solar cells also known simply as dye solar cells (DSC) are photoelectrochemical devices that aim at easier manufacturing and cheaper materials compared to traditional solar cells. One of the most expensive components of a conventional DSC are the transparent conducting oxide (TCO) coated glass substrates which make up to 60 % of the total material costs of DSCs.¹ Hence investigation of cheaper substrate materials is highly motivated. When using typical electrolyte with a tri-iodide/iodide redox couple, the corrosiveness of the electrolyte limits the options of stable substrate materials tremendously.²⁻⁸ Only titanium and some other expensive metals have been shown to be stable in the aging test of complete dye solar cells without a protective coating.^{4,6} The application of a protective coating is one method to improve the range of suitable materials,^{4,9} but they add to the cost both from materials and manufacturing perspective. Changing the electrolyte to a less corrosive one is another option to enable the use of less costly materials which is the focus in this paper.

There are various alternative redox couples available and the most interesting among them are the cobalt complex based electrolytes as they have resulted in a record breaking efficiency of over 12 %.¹⁰ The investigation of this topic has boomed since Feldt et al. reported how to design dyes to work with the cobalt complex redox couple to reach high efficiencies.¹¹ In a previous study it was shown that cobalt complex electrolytes are not completely non-corrosive but instability was seen in the case of several metals including copper, zinc and aluminum.¹² In that study the cheapest metal that was as stable as TCO glass was stainless steel (StS) 304.¹² StS 304 is one of the cheapest nickel containing

stainless steels and it has been estimated to be 10-60 % cheaper than glass with TCO coating of fluorine doped tin oxide (FTO).^{1,13} In this contribution we aim to further significant cost reductions by applying a cheap ferritic stainless steel. Ferritic stainless steels (here after referred simply as ferritic steel) do not contain nickel like stainless steel 304 but have instead a higher content of iron. Ferritic steel EN 1.4016 was chosen here as it is a very commonly used ferritic steel grade and it is about 35% cheaper than StS 304.¹⁴

Here the low cost ferritic steel is investigated in terms of performance and corrosion stability in dye solar cells with cobalt complex based electrolyte. The ferritic steel is employed as a substrate for the counter electrode. In the previous study, it was shown that metals generally do require a catalyst layer when used with cobalt complex electrolyte and low temperature platinization worked well with metallic substrate whereas thermal platinization and polymer catalysts were good on FTO glass.¹² Therefore in this contribution we use also low temperature platinization on the ferritic steel substrates and thermal platinization for the glass substrates. The corrosion stability of the ferritic steel is investigated by aging complete dye solar cells. This gives direct information of the corrosion in the actual device. Besides performance analysis and visual inspection, a scanning electron microscope analysis is made to investigate if there were any marks of corrosion on the metallic substrate.

2. Experimental methods

The photoelectrodes consisted of a TiO₂ film deposited on fluorine-doped tin oxide (FTO) coated glass substrate (15 Ω/sq.). The photoelectrodes had a compact TiO₂ spray underlayer prepared at 450 °C according to literature.¹⁵ The porous TiO₂ layer composed of two layers which were screen printed with mesh 63T: 4 μm thick transparent TiO₂ layer (DSL 18NR-T, Dyesol) and 4 μm thick TiO₂ layer with reflecting particles (DSL 18NR-AO, Dyesol). The electrodes were sintered at 450 °C for 30 min, then a TiCl₄ treatment was applied and that was followed by yet another sintering at 450 °C for 30 min.¹⁶ The photoelectrodes were dyed with 0.3 mM Z907 (cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II), Dyesol) in 1:1 acetonitrile / tert-butanol as it has been found to work well with cobalt complex electrolyte.¹⁷

A low temperature chemical platinization was done on the ferritic steel substrates (EN 1.4016, Outokumpu) using a recipe modified from Chen et al.:¹⁸ 0.5 mL of platinum solution (1g of H₂PtCl₆ in 100 mL of 4 % HCl) was mixed with 11 mL water and then the substrate was immersed in the resulting solution at 70 °C for 12 minutes. The counter electrodes for the reference FTO glass cells were made by spreading 4 μl of 10 mM H₂PtCl₆ in 2-propionitrile on each FTO glass counter electrode substrate which were then heat treated at 390 °C for 15 min.

A 25 μm thick Surlyn (1702) polymer spacer was used to seal the electrodes together. The cobalt complex electrolyte (here after also called cobalt electrolyte) consisted of 0.2 M [Co(bipy)₃](PF₆)₂, 0.04 M [Co(bipy)₃](PF₆)₃, 0.5 M 4-tert-butylpyridine and 0.1 M LiClO₄

in acetonitrile (ACN) and the cobalt complexes were synthesized according to literature.¹⁷ In the reference glass cells, a commercial iodine based electrolyte (HSE-EL) by Dyesol (here after also called iodine electrolyte) was employed. The electrolyte filling holes were on the counter electrode glass in the reference glass cells. In the cells with ferritic steel as the counter electrode, the holes were on the glass photoelectrode. The holes were in both cases closed with Surlyn polymer foil and a thin cover glass.

The photovoltaic performance was measured with a solar simulator providing 1000 W/m² AM1.5G equivalent light intensity (1 Sun) on a black surface. The cells were aged under approximately 1 Sun equivalent illumination using halogen (Philips, type 13117) lamps at 40 °C for 1 month (i.e. 700 hours).

Incident photon to collected electron (IPCE) measurements and optical transmittance measurement were done using IPCE measurement system QEX7 by PV Measurements Inc. The IPCE measurements were done using DC mode. The spectra were recorded in the range of 300-1000 nm with 10 nm intervals.

Electrochemical impedance spectroscopy (EIS) measurements were conducted on the complete dye solar cells. EIS measurements were conducted firstly at 1 Sun conditions at open circuit condition and additionally in dark on a range of voltages from 0 V to 0.7 V at 100 mV intervals. All the measurements were made in potentiostatic mode, using amplitude of 10 mV and over the frequency range of 0.1 Hz – 100 kHz. The equivalent circuit fitting of the resulting EIS spectra was conducted with Zview2 software.

Scanning electron microscopy (SEM) analysis was done on the aged cells with a Zeiss Ultra 55 field emission scanning electron microscope. The part of the substrate outside the active area (approximately 0.4 cm², i.e. area in contact with the electrolyte) served as a reference when evaluating changes caused by the electrolyte. An elemental analysis for investigation of corrosion residues was done with the SEM using a Bruker AXS energy dispersive X-ray spectroscopy (EDS) equipment and Quantax 400 software. In the SEM measurements a 10 kV accelerating voltage was used.

3. Results and discussion

3.1. Photovoltaic performance

Table 1. Average photovoltaic parameters and their standard deviations for the different types of cells.

	number of cells	i_{sc} [mA/cm ²]	V_{oc} [mV]	FF [%]	η [%]
ferritic, cobalt	5	10.2 ± 0.7	790 ± 10	56 ± 7	4.5 ± 0.4
glass, cobalt	4	11.9 ± 0.3	781 ± 15	56 ± 5	5.3 ± 0.6
glass, iodine	3	14.7 ± 1.5	670 ± 6	51 ± 4	5.1 ± 0.9

The photovoltaic performance shows (Figure 1 and Table 1) that the cells with the ferritic steel counter electrodes gave almost as good performance as the reference glass cells with the same electrolyte. The difference between those cells is in the short circuit current density i_{sc} while open circuit voltage V_{oc} and fill factor FF are basically the same for both cell types with cobalt electrolyte. The highest efficiency measured from a cell with the ferritic steel counter electrode was 5.04 % which is over 2.5 times higher compared the

previously best cell with metallic counter electrode substrate and cobalt electrolyte.¹² Compared to that previous study, here the photoelectrode structure was improved as there were TiO₂ blocking layer on the FTO-glass substrate and reflecting particles in the porous TiO₂ film as well as a different electrolyte composition. If a more sophisticated dye was used such as that introduced by Yella et al.¹⁰ instead of the commercial that was applied here, probably even higher efficiencies could be reached with the cells using cobalt complex electrolyte.

Interestingly the glass cells with the cobalt and iodine electrolytes gave similar efficiencies (Figure 1 and Table 1) even though there are differences in the other parameters. V_{OC} is more than 100 mV higher in the cobalt cells compared to the iodine cells. The cobalt cells have a higher FF and the maximum point is more than 100 mV higher compared to the iodine cells. The major benefit of using cobalt complex electrolyte is that the electrolyte redox energy level is lower with this type of cobalt complex electrolyte than with iodine electrolyte resulting in possibility to reach higher V_{OC} with a given dye.¹⁹ Therefore the higher V_{OC} with cobalt electrolyte was to be expected from that perspective.

The photocurrent on the other hand is higher in the iodine cells than in the cobalt cells (Figure 1 and Table 1). One factor that could potentially affect photocurrent in the cobalt cells is the current density limitation. Thus the limiting current was measured using symmetrical counter electrode – counter electrode cells. The limiting current density was measured to be 17 ± 2 mA/cm² in the cobalt electrolyte and above 40 mA/cm² in the iodine electrolyte. Thus in both cases the limiting current density was well above measured i_{SC} in

the respective type cells (Table 1) which means it should not have a significant effect on i_{SC} . The factors affecting the photocurrent are analyzed in more detail in the following sections using IPCE and EIS measurements.

3.2. Analysis of the photocurrent with IPCE

The investigation is focused here in the differences between the two cell types with cobalt complex electrolyte. Since the only difference between the cobalt cells is the different counter electrodes (they have similar photoelectrode and electrolyte), there are only a limited number of factors that can affect the photocurrent. Thus, for instance, there should not inherently be any differences in electron injection efficiency. Firstly, the counter electrode could affect the optics i.e. light harvesting. Secondly, there could be potentially also an effect to electron collection if some catalyst particles were detached from the counter electrode and ended up to the photoelectrode where they would increase the recombination.

In the range 300-600 nm the cobalt ferritic cell has a slightly smaller ~5% quantum efficiency (QE) compared cobalt glass cells (Figure 2a). Such a lowering is likely due to the sealing on the photoelectrode side which causes such optical losses compared to the glass cells which were sealed from the counter electrode side. It is important to note that the photoelectrodes had reflecting particles in them and they were thus non-transparent and therefore no significant back reflection from counter electrode was to be expected. The difference in the photocurrent between those two cell types was a bit larger in the IV measurements, about 15 % (Table 1), compared to the difference in the IPCE, about 5%.

The IV and IPCE measurement that were used in this measurement have a bit different optical setup and geometry e.g. the former is composed on multiple lamps and the latter of one. In the IV measurements there can easily be so called edge effects which are caused by geometrical differences which here are related to the glass counter electrode being thicker and transparent allowing a larger portion of reflected light to enter the photoelectrode as Figure 3 illustrates. The IPCE measurements employ a narrow monochromatic beam focused in the center of the photoelectrode film and thus the edge effects are negligible in that case. Hence it seems possible that the difference in i_{sc} in the IV measurement could have come from edge effects. The edge effects get smaller as the cell size is increased and they are basically a measurement error when considering the scalability of the results. On the positive side, if the edge effects are the cause for the differences in the photocurrent as it seems, it would mean that the cells with ferritic steel and TCO glass based counter electrodes would not have much difference in the performance in a large scale device.

In regards of the possible differences in the electron collection between the cobalt cells, the decreases in the electron collection typically lower the quantum efficiency at the long wavelengths more than at the short ones. This is because the long wavelengths are absorbed further from the electrical contact of the photoelectrode than the short wavelength photons and as the mean distance of injected electrons to the contact increases, so does the recombination losses decreasing the collection efficiency of electrons. Here the shape of the IPCE curve is similar in both cobalt cells which suggests that there would not be significant differences in electron collection between those cells. The effects of the ferritic

counter electrode on the recombination at photoelectrode are investigated in more detail using EIS measurements in Section 3.4.

Let us consider next the differences between glass cells with cobalt and iodine electrolytes. In the wavelengths below 420 nm the cobalt cells gave higher QE compared to iodine cells (Figure 2a). Based on the transmittance data of the electrolytes encapsulated between clear microscope glass sheets (Figure 2b), it is apparent that this effect is caused by the absorption of light by iodine i.e. iodine transmits less light at the low wavelengths. It can be deduced that differences in light harvesting efficiency cannot explain lower i_{SC} of cobalt cells compared to the iodine cells.

Literature shows that the electron recombination from the TiO_2 to the electrolyte has often been significantly larger in the cobalt electrolyte compared to the iodine electrolyte.²⁰ Thus a likely hypothesis is that the cobalt cells could have issues with the electron collection. In the case of cobalt electrolyte, the charge transfer process is one electron reaction and due to that it is more prone to current leakage compared to the iodine electrolyte which involves two electrons in the charge transfer process. Figure 2a shows that at the peak of the QE curve i.e. at 530 nm, the iodine electrolyte has 15 % higher QE compared to the cobalt electrolyte. The difference is, however, even greater in the longer wavelengths as at 700 nm the difference is 35 %. Such wavelength dependence in the QE data suggests that the cobalt cells have quite likely a lower electron collection efficiency compared to the iodine cells. It seems probable that the better electron collection is the reason for the higher

photocurrents in the iodine cells also in this study. The EIS measurement are made to investigate the differences in the electron lifetime in Section 3.4.

3.3. EIS analysis of the charge transfer at the counter electrode

The comparison of the charge transfer at counter electrode R_{CT} and the diffusion resistance in the electrolyte W_d at the electrolyte/counter electrode interface is studied here. The investigation of R_{CT} and W_d is done under illumination and at open circuit since in that state 1) their response is clearly visible and 2) there is no current going through the cell so the counter electrode/electrolyte interfaces has zero potential difference over them meaning that they are all in similar state and thus the data from the different cells can be quantitatively compared. The equivalent circuits used in this work are the same as used in our previous work.²¹ Examples of the measured data and the corresponding fits are given in Figure 4.

Table 2. Average EIS characteristics and their standard deviation under illumination at open circuit of all the studied cells.

	R_{CT} [Ωcm^2]	W_d [Ωcm^2]
ferritic, cobalt	8 ± 3	4.1 ± 0.6
glass, cobalt	4.8 ± 0.9	3.9 ± 0.9
glass, iodine	5 ± 3	1.2 ± 0.2

The charge transfer resistance is on average 50 % higher for the ferritic counter electrodes compared to the glass based counter electrodes (Table 2). There was more deviation in the catalytic performance of the ferritic counter electrodes compared to glass based counter electrodes with cobalt electrolyte (Table 2). Interestingly, the best ferritic counter electrode

ones gave as low as $3.6 \Omega\text{cm}^2$ resistance which is actually as low as the best glass counter electrode which also gave $3.6 \Omega\text{cm}^2$. This shows that the ferritic counter electrodes can be as efficient as the glass based ones.

The iodine cells have 3-4 times lower W_d than the cobalt cells (Table 2). This suggests that the diffusion of the charge carriers in the cobalt electrolyte is more sluggish than in the iodine electrolyte. The cobalt complexes are much more bulky compared to the tri-iodide and iodide and thus their diffusion coefficient is lower which gives a higher diffusion resistance W_d . Furthermore, the cobalt electrolyte has acetonitrile as the electrolyte solvent while the commercial high stability electrolyte has 3-methoxypropionitrile. The former is much less viscous than the latter and diffusion coefficient of the charge carrier is higher.²² This means that difference in diffusion of the ions caused by purely by the differences in the charge carriers would most likely be even larger if the same solvent was used in both electrolytes.

3.4. Analysis of the charge transfer at the photoelectrode

The ferritic cobalt cells had a bit lower photocurrent compared to the glass cobalt cells and based on the IPCE section, it seems likely that was due to different optical effects and not differences in the electron collection. In this section further investigations are made to find out whether or not the ferritic counter electrode has affected the performance of the photoelectrode. One way that counter electrode could decrease the photocurrent is if catalyst particles detach and deposit at the photoelectrode where they would increase electron recombination.

The cobalt cells with the ferritic counter electrode and the FTO-glass based counter electrode have similar EIS response for the photoelectrode in respect to all studied parameters (Figure 5) i.e. most cobalt cell data overlap when taking into account the standard deviation. In those cells the photoelectrode and the electrolyte were similar so this result was expected, but at the same time it confirms that the ferritic counter electrode has not affected the electrochemical characteristics of the photoelectrode (e.g. by hypothesized detached catalyst particles) and that the decreased i_{SC} of the ferritic cobalt cells compared the glass cobalt ones must be only due to the optical effects that were discussed in the IPCE section.

The cells with iodine electrolyte are again much different compared to the ones with the cobalt electrolyte: Firstly, R_{PE} is actually smaller (Figure 5a) with iodine electrolyte compared to cobalt electrolyte. Secondly, CPE_{PE} is instead larger in iodine electrolyte than with cobalt (Figure 5b). The effective electron lifetime at the photoelectrode τ is in the large negative voltages similar in both electrolytes (Figure 5c), but there are differences at the small negative voltages. Even though the cobalt electrolyte does not have any problems in R_{PE} and electron lifetime when comparing to the iodine electrolyte, the results need to be evaluated in terms of the R_T values as well to evaluate possible effects to the electron collection. The ratio between the electron diffusion length L and the thickness of the TiO_2 film d is:^{23,24}

$$\frac{L}{d} = \sqrt{\frac{R_{PE}}{R_T}} \quad (\text{Eq. 1})$$

R_T value can be determined with good accuracy only at few voltages points on the studied spectra as is known from the literature:²⁴ At high negative voltages the counter electrode response overruns R_T . At low negative voltages, the recombination from the substrate instead of that from the TiO_2 dominates the response and R_T which is related to the charge transfer at the TiO_2 is not shown either in the data. In the iodine cells the L/d ratio of all the points that could be evaluated with high accuracy was 3.4 ± 0.7 . In other words the diffusion length was about triple compared to the actual length of the film and that is generally regarded as high enough ratio to gain high electron collection efficiency. In the cobalt cells there were often Gerisher type responses²⁴ meaning that R_T and R_{PE} could not be credibly decoupled,²⁵ and that the L/d ratio was in those cases below 1 and the highest measured value for the ratio was 1.3. When the electron diffusion length is smaller than the electrode thickness, it is evident that not all the electrons can be collected. Even if the ratio is a little above 1, there are still significant electron collection losses. These electron diffusion length results suggest that there would be significant electron collection losses in the cobalt cells whereas they would be minor in the iodine cells. These conclusions agree with the IPCE data which also suggested that there would be larger electron collection losses in the case of cobalt compared those in iodine.

3.5. Stability of counter electrode made on ferritic steel

From the literature it is known that the overall stability of cobalt cells is still an issue even with glass substrates which do not corrode and generally these kind of cells have remained stable only for 200 h under illumination at moderate temperature (up to 40 °C).^{10,12} Here

the focus is not if cobalt based cells are stable or not, but does the cobalt electrolyte corrode ferritic steel or not. Previous study has shown that even cobalt complex electrolyte can corrode some metals such as copper and zinc.¹² In this study the cells were aged at 40 °C in approximately 1 Sun illumination for 700 hours. At such a moderate temperature, the volatile ACN solvent that was employed in the cobalt electrolyte is known to be stable.²⁶

In the both types of cobalt cells i.e. with ferritic and glass counter electrodes, i_{SC} has dropped on average more than 50 % during aging of 700 hours (Figure 6). FF has also decreased in the cobalt cells and there is a huge variation in FF within each cell type (Figure 6). In contrast, V_{OC} has remained at about 90 % level of the original (Figure 6). Figure 6 shows that the efficiency of the cobalt cells is decreased on average 60-70 % because of all of the above mentioned factors but the main reason for this are the losses in i_{SC} . The average efficiency drop in the ferritic cobalt cells is somewhat higher compared to that of the glass cobalt cells. However, due to the large standard deviations after aging, the IV measurements were unfortunately inconclusive whether there is a difference between the stability of the two types of cobalt electrolyte cells. Since the degradation was substantial in both types of cobalt cells, more information is needed to verify that there was no corrosion and for that purpose the visual inspection and microscopic analysis of the aged samples was also made and it is discussed below.

In contrast to the cobalt cells, the average of each performance characteristic in the iodine cells remained close to 1 (Figure 6). Thus it can be said that the aging issues of the cobalt

cells are related to the cobalt electrolyte and the overall stability related to the cobalt electrolyte needs improving as was known from the literature.^{10,12}

In the visual inspection of the cells after the 700 hours of aging, there were no apparent colour changes in the cells. A common occurrence in the case of corrosion are changes in the electrolyte colour as corrosion typically consumes the only colourful electrolyte component i.e. yellow redox couple^{2,3,5,7,8} and/or results in a non-transparent corrosion product (typically very dark) that can be dispersed in the electrolyte or accumulated on the surfaces.^{5,12} In the literature in the case of iodine electrolyte, the visual change of the electrolyte colour has actually been so clear that it has been used for tracking the progression of corrosion.⁷ The cobalt electrolyte has a much more pale color compared to iodine electrolyte which makes the tracking of corrosion electrolyte color more difficult. But even in the case of cobalt electrolyte, non-existence of visible changes is a sign of corrosion not occurring.

The visual inspection also showed an improvement in the cobalt cells as there was no visible detachment of dye in this study. The detachment of the dye was a significant problem in our previous study with the cobalt electrolyte.¹² Here, the electrolyte was prepared in a different way and the major difference was that no NOBF_4 was needed. It seems likely that in that previous study the dye desorption was related to the presence of NOBF_4 . Further development of the cobalt electrolyte is, however, still needed to stabilize the performance of the cells from other perspectives.

The aged cells were disassembled and inspected with SEM to get a microscopic view on the aged surfaces. According to the literature in the cases of corrosion, there have been clear marks such as corrosion pitholes on the corroded substrate itself and/or presence of apparent corrosion products elsewhere in the cells (i.e. on the other electrode).⁴⁻⁶ Here, the SEM images did not reveal any marks of corrosion in the surface of the aged ferritic steel as the example in Figure 7 shows. Furthermore, the elemental analysis combined to SEM imaging did not show any apparent corrosion products at the other electrode (i.e. the glass based photoelectrode). The SEM image of the ferritic steel counter electrode (Figure 7) also shows that the Pt particles did not give a high coverage of the surface but most of the metal surface was exposed to the electrolyte as intended here. This is a very important detail when evaluating the stability of the metallic substrate/electrolyte interface – a dense Pt layer completely covering the CE substrate could act as a corrosion protection coating preventing interaction of the substrate metal itself with the electrolyte thus masking the effects of potential corrosion to an unknown degree. Here, we can rule out such possibility and take the results representative of the corrosion stability of the ferritic steel substrate.

As an overall result, it appears that ferritic steel did not corrode in the cobalt electrolyte as the performance analysis, visual inspection and most importantly SEM analysis did not show any marks of corrosion. The challenges lie in improving the overall stability of the cobalt electrolyte cells. This would also allow a more detailed analysis of the aging behaviour of the cells as a whole as well as from the perspective of new candidate counter electrode materials. Nevertheless, the absence of the hallmark corrosion indicators (electrolyte bleaching, corrosion pits on the metal and products of the corrosion reaction)

in the degraded cells means that we can consider the ferritic steel an interesting low cost candidate material for metal based DSSCs employing cobalt electrolytes.

4. Conclusions

A low cost metal, ferritic stainless steel, was introduced as an alternative to expensive TCO-glass for a counter electrolyte substrate when using cobalt complex electrolyte. The ferritic stainless steel is approximately 35 % cheaper compared to StS 304 which was previously the cheapest metal not to corrode in cobalt electrolyte. The best cell with ferritic steel counter electrode resulted in efficiency of 5.0% which was more than 2.5-times higher compared to previously reported values in the case of metal substrate and cobalt complex electrolyte. The best ferritic counter electrode gave equally low charge transfer resistance compared to the glass based counter electrodes. Furthermore the ferritic cells did not show any signs of corrosion in the aging test, which is an important finding as many other low cost metals have suffered from corrosion in the cobalt complex electrolyte. Therefore it can be concluded that a very low cost metallic substrate has been found that both works well and is apparently not corroded by the cobalt electrolyte in complete DSC within 700 hours continuous light soaking at 1 Sun. However, the overall stability of the cells with cobalt electrolyte is still a challenge and requires further investigation.

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Figure captions

Figure 1. IV curves of the best performing cells. The efficiencies were 5.04 % for the ferritic cobalt cell, 5.91 % for the glass cobalt cell and 5.97 % for the glass iodine cell.

Figure 2. a) Example external quantum efficiency (EQE) curves in the three different DCSs which had i_{SC} values near the average of respective cell type. b) The transmittance of the electrolytes encapsulated between clear glass sheets.

Figure 3. Schematic illustration of possible edge effects when using indirect light in the case of different counter electrode substrates (not in scale). When using a metallic substrate, the light reflects directly from the inner surface of the substrate. In the case of transparent electrodes, the light can reflect from the outer surface of the metal. Hence with certain angles the light can still be reflected back to the dyed TiO₂ in glass cells while in the cells with metallic counter electrode substrate it would not be possible.

Figure 4. Example of the EIS responses of the different types of solar cells measured under illumination at open circuit conditions. The measured data is shown with markers and their fits with continuous lines in the respective color. The EIS data is plotted in a) Nyquist plot, b) imaginary impedance (Z'') as a function of frequency f and c) real impedance (Z') as a function of f .

Figure 5. The average and standard deviation of a) charge transfer resistance at the photoelectrode / electrolyte interface R_{PE} , b) capacitance related to that resistance photoelectrode C_{PE} , and c) effective electron lifetime τ in case of three types of studied cells. The data was measured in dark as a function of cell voltage.

Figure 6. The average and standard deviation of the normalized performance characteristics after 700 hours of aging for each cell type. The comparison point in the normalization was the initial performance of each cell shown in Table 1.

Figure 7. Example SEM image of the aged ferritic counter electrode. In this image the light colored particles are Pt and the grey back ground surface is the ferritic steel.

Figure 1.

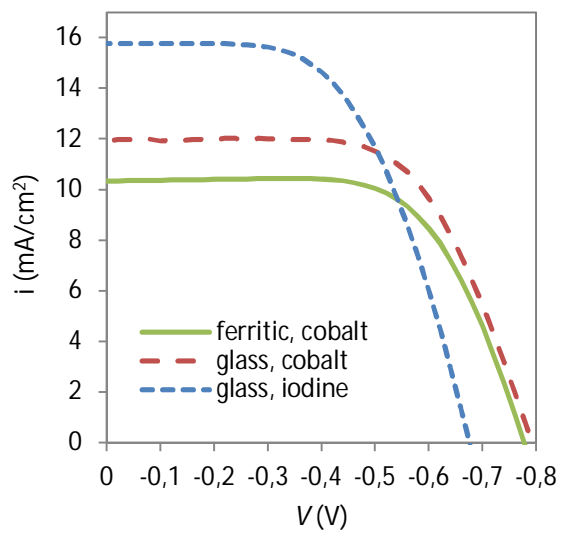


Figure 2.

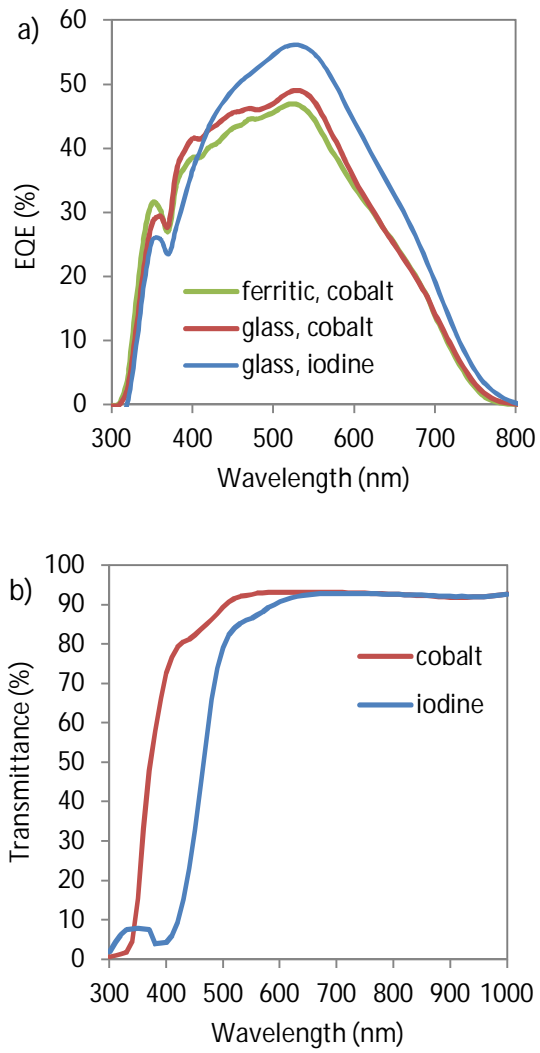


Figure 3.



Figure 4.

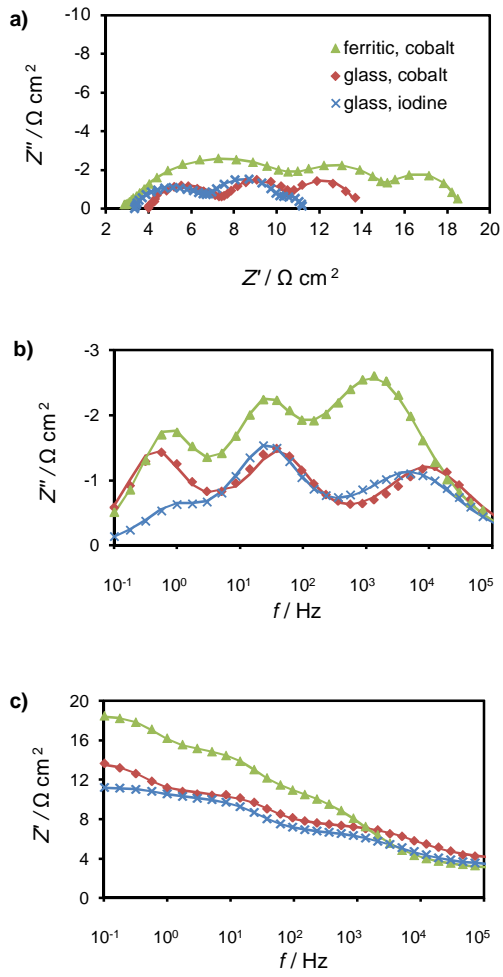


Figure 5.

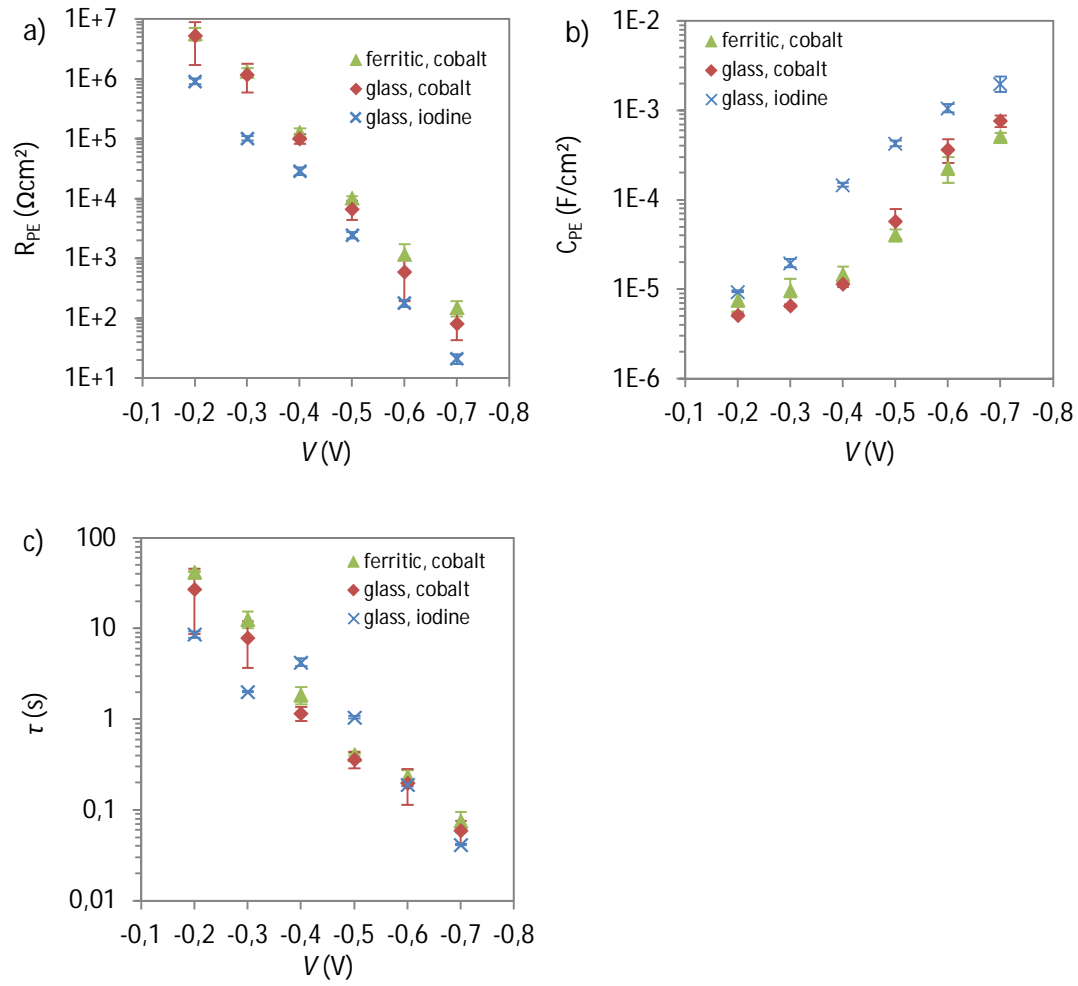


Figure 6.

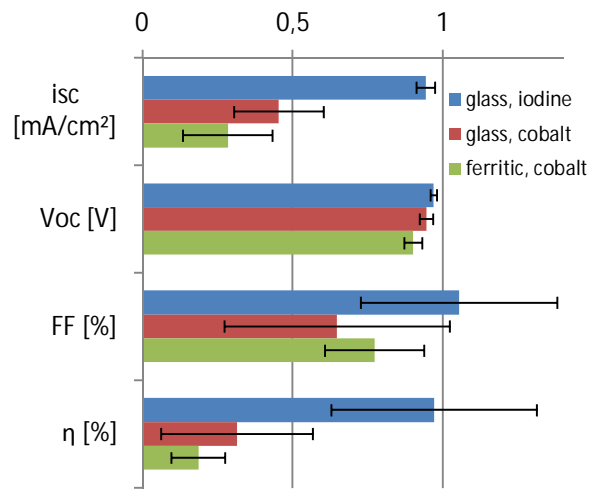


Figure 7.

