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Do counter electrodes on metal substrates work with cobalt complex based electrolyte in dye sensitized solar cells?

Kati Miettunen^{,a,b}, Tapio Saukkonen^c, Xiaoe Li^b, ChunHung Law^b, Yeo Kee Sheng^b,
Janne Halme^a, Armi Tiihonen^a, Piers R. F. Barnes^b, Tarek Ghaddar^d, Imran Asghar^a,
Peter Lund^a, Brian C. O'Regan^b*

^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

^d American University of Beirut, Department of Chemistry, Beirut, 11-0236, Lebanon

* Corresponding author: Telephone: +358 9 451 8253.

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

Abstract

Yes. Testing 7 different metals as a substrate for a counter electrode in dye sensitized solar cells (DSSC) showed that some metals can be a good option for use with cobalt electrolyte. It was found that Stainless steels 304 and 321 as well as Ni and Ti suit well to the counter electrodes in DSSCs with cobalt electrolyte. In these 4 cases both the efficiency and the lifetime were similar to the reference cells on conducting glass substrates. In contrast, the cells with Al, Cu and Zn substrates suffered from both a low efficiency and a poor stability. These three metals had clear marks of corrosion such as apparent corrosion products in the aged cells. Additionally, we also investigated how the different types of catalyst materials perform in the case of a metal counter electrode (stainless steel 304) with cobalt electrolyte in comparison to reference glass cells. Among the 5 different catalyst layers the best results for stainless steel electrode were achieved with low temperature platinization whereas polymer catalysts poly(3,4-ethylenedioxythiophene)-*p*-toluenesulfone and poly(3,4-ethylenedioxythiophene)-polystyrenesulfone that worked well on the glass worked very poorly on the metal.

Keywords: Metals; Stability; Redox couple, Corrosion

1. Introduction

Dye sensitized solar cells (DSSCs) also known as dye solar cells are relatively new photovoltaic devices whose potential advantages include easy manufacturing and cheap materials. To improve the competitiveness of the DSSC technology, further cost reductions are needed. One of the most expensive part of the conventional DSSCs are the glass sheets coated with transparent conducting oxide (TCO).^{1,2} Using metal as a substrate for one of the electrodes can result in major cost reductions: for instance Al films cost 100-times less than the TCO glass sheets.³ Furthermore metal films have 3-4 orders of magnitude lower sheet resistance compared to the TCO glass ^{4,5} and they also enable roll-to-roll mass production. The challenge with metals is their stability, as most metals corrode in iodine containing electrolyte.⁴⁻⁸ In the case of no protective coatings on the metallic counter electrode, only expensive Ti based cells have systematically passed 1000 h in light soaking.⁸ A corrosion blocking layer such as a sputtered Pt layer can improve the stability in the case of many metals, but even that is not sufficient if the metal is highly prone towards corrosion.⁸ In particular the cheap metals are often prone to corrosion and to enable their use without costly coatings, a non-aggressive electrolyte is needed. One approach is to change the redox couple.

Using cobalt complexes instead of iodine is currently a hot topic in the DSSC field and very high efficiencies (even over 12 %) have been recently published with cobalt.⁹⁻¹² Alternative redox electrolytes are often marketed as non-corrosive, but no stability tests of metals in complete devices have been presented. As iodine based electrolyte is highly

corrosive, it is likely that the alternative electrolytes are less corrosive. However, that does not guarantee that all metallic electrodes would remain stable in them in particular in operational conditions.

The purpose of this work is to investigate the stability of metals in cobalt based electrolyte that has received a lot of attention. Here we examine the potential of 7 different metals to be used as substrates for counter electrode in DSSCs with cobalt electrolyte. The 7 different metals (Al, Cu, Zn, Ni, Stainless steel (StS) 304, StS 321, and Ti) were selected for various different reasons: some (e.g. Al and StS) could be used as the substrate itself, some (e.g. Zn) are often used as coatings whereas some (e.g. Cu) have superior conductivity for current collecting grids. Many of them have been suggested for dye solar cells earlier to be used with iodine based electrolyte.³⁻⁸ Earlier studies have also shown that electrolyte soaking test are not sufficient proof of stability, because the operational conditions of a device affect the degradation of the cell e.g. by changing the polarization at the electrodes.^{8,13} The electrolytes used in dye solar cells are quite specific and there are no galvanic series let alone Pourbaix diagrams for such electrolytes that could be used to predict which metals corrode and in which potential. Our previous studies have shown that the easiest way to test the suitability of a certain metal/electrolyte combination is to test in the real conditions. Thus herein the metals are employed directly in operational DSSCs to study their performance and stability.

Both the substrate material and the redox electrolyte affect which type of a catalyst layer works best or if one is needed at all. Therefore here selection of metal substrates is

studied without a catalyst layer and with a set of different catalyst layers in the cells filled with cobalt electrolyte. Five different catalyst layers were selected: high temperature Pt, low temperature chemical Pt, porous carbon as well as two different conducting polymers. High temperature thermal platinization is a conventional method to make a highly performing and very stable catalyst layer on TCO glass based electrodes. In contrast, low temperature platinization has been a better option for metallic counter electrodes at least in the case of iodine based electrolytes.^{4,8} Both the carbon and the polymer catalysts have been identified to be as good as, or even better, catalysts layers than the traditional high temperature Pt in the case of TCO glass when using cobalt electrolyte.^{12,14} Thus there are many catalyst options that could work and testing is needed to find which type of catalysts work best in this case. The aim here is to screen the different metallic substrates and the catalyst materials in order to identify the most promising combinations for further investigation, optimization, and use with a cobalt electrolyte in DSSCs.

2. Experimental methods

The photoelectrodes consisted of a TiO₂ film deposited on fluorine-doped tin oxide (FTO) coated glass substrate (15 Ω/sq.). The TiO₂ paste was made by diluting a commercial TiO₂ paste (DSL 18NR-T, Dyesol) with terpinol in 2:1 ratio of paste and terpinol. The electrodes were sintered at 450 °C for 30 min, then a TiCl₄ treatment¹⁵ was applied and that was followed by yet another sintering at 450 °C for 30 min. The resulting 5.2 μm thick TiO₂ films were sensitized using a dye solution consisting of 0.3

mM TG6 dye (i.e. cis-bis(thiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato){4,4'-bis[2-(4-hexylsulfanylphenyl)vinyl]-2,2'-bipyridine}ruthenium(II) mono(tetrabutylammonium) salt) in 1:1 ratio of ethanol and chloroform. The catalyst was an 8 μm thick porous layer of carbon gel¹⁶ (if not otherwise mentioned) which was deposited on the different metals (listed in Table 1) and reference FTO glass. All the metals were purchased from Goodfellow. The electrodes were sealed with a 25 μm thick Surlyn (1702) polymer spacer. The area defined by the spacer was about double compared to the size of the dyed TiO_2 layer and the carbon layer to leave an window area to monitor changes in the color of the metal surface and the electrolyte. The cobalt electrolyte consisted of 0.3 M $[\text{Co}(\text{bipy})_3](\text{PF}_6)_2$, 0.1 M NOBF_4 (Aldrich, 175064), 0.5 M 4-tert-butylpyridine (tBP, 99 %, Aldrich, 142379) and 0.1 M LiClO_4 (98%, Lancaster, 15713) in methoxypropionitrile (MPN). $[\text{Co}(\text{bipy})_3](\text{PF}_6)_2$ was synthesized as described in literature.⁹ In some of the reference cells, an iodine electrolyte was employed and that consisted of 0.3 M benzimidazole (BI, Aldrich, 98 %), 0.05 M Guanidinium thiocyanate (GuSCN, Fluka \geq 99 %), 0.8 M PMII (PMII, AlfaAesar, 98 %), and 0.05 M with I_2 (Sigma-Aldrich, \geq 99 %) in MPN. The electrolyte was inserted through filling holes in the glass photoelectrode substrate that were then sealed with another Surlyn polymer foil and a thin cover glass.

In Section 3.4 different catalyst layers are investigated besides the carbon gel: Thermal Pt 5 mM solution in 390 $^\circ\text{C}$ for 20 min. Chemical platinization was done according to Chen et al.:¹⁷ mixing 1 mL of platinum solution (1g of H_2PtCl_6 in 100 mL of 4 % HCl) with 11 mL water and plating the film in the solution at 70 $^\circ\text{C}$. One of the polymer catalyst layers was made by spin coating 3 layers of 0.5 wt.% poly(3,4-ethylenedioxythiophene)-*p*-

toluenesulfone (PEDOT-TsO) in nitromethane (Aldrich, 649821) with 700 RPM speed similar to our previous studies.¹⁸ The other polymer catalyst, poly(3,4-ethylenedioxythiophene)/polystyrenesulfone (PEDOT-PSS) (H. C. Starck, P VP AI 4083), was also spin coated but that required a higher speed (2500 RPM) to disperse. This set of cells in Section 3.4 was dyed with 0.3 mM Z907 (cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II)) in acetonitrile / tert-butanol (1:1) solution and had also a TiO₂ spray under layer.¹⁹

Table 1. Descriptions of different metals used in this study.

Substrate	Description	Thickness (mm)	Product number
Al	99.0 % Al	0.05	AL000490
Zn	99.95 % Zn	0.1	ZN000250
Cu	99.99 % Cu	0.05	CU000491
Ni	99.98 % Ni	0.05	NI000391
StS 304	Fe/Cr 18/Ni 10	0.05	FE220250
StS 321	Fe/Cr 18/Ni 9/Ti	0.05	FE210250
Ti	99.6 % Ti	0.1	TI000370

The photovoltaic performance was measured with a solar simulator providing 1000 W/m² AM1.5G equivalent light intensity (1 Sun). The cells were aged under approximately 1 Sun equivalent illumination using a fluorescent lamp (type Solara from ANCO) at approximately 40 °C for 500 h.

Electrochemical impedance spectroscopy (EIS) was used in the examination of the charge transfer resistance at the metal substrate / electrolyte interface. The EIS measurements were conducted using IM6 Impedance measurement unit by Zahner Elektrik. The EIS measurements for the substrate – counter electrode samples were here conducted in dark, in potentiostatic mode at 0 V, using amplitude of 10 mV and over the frequency range of 0.1 Hz – 100 kHz. Zview2 software was used in the fitting of the equivalent circuit.

Scanning electron microscopy (SEM) images were taken of the aged cell components using a Zeiss Ultra 55 field emission scanning electron microscope to investigate possible changes. The SEM was equipped with Bruker AXS energy dispersive X-ray spectroscopy (EDS) equipment and Quantax 400 software which were used for the analysis of the elemental composition. A 10-15 kV accelerating voltage was employed in the SEM imaging.

3. Results and discussion

Firstly it was studied if the substrates would work as such i.e. without a catalyst layer as counter electrodes. For this purpose cells containing the bare substrate on one side and a platinized glass on the other side were made. These cells were then studied with EIS to determine the charge transfer resistance at the substrate / electrolyte interface R_{CT} . Table 2 contains the measured R_{CT} data. It is generally considered that a good counter electrode has R_{CT} less than $10 \Omega\text{cm}^2$. Here most of the substrates had R_{CT} higher than $1000 \Omega\text{cm}^2$

(Table 2) which in practice means that they cannot be used as counter electrodes without an additional catalyst layer. The lowest R_{CT} ($150 \Omega\text{cm}^2$, Table 2) was measured with Ni substrate but even in its case a catalyst layer is required for achieving good performance at standard measurement conditions.

Table 2. Typical charge transfer resistances at the metal electrode / electrolyte interface without a catalyst layer.

Substrate	$R_{CT} (\Omega\text{cm}^2)$
Al	$2.9 \cdot 10^7$
Zn	$1.0 \cdot 10^5$
Cu	$1.6 \cdot 10^4$
Ni	$1.5 \cdot 10^2$
StS 304	$3.4 \cdot 10^5$
StS 321	$1.8 \cdot 10^5$
Ti	$4.3 \cdot 10^3$

3.1. *Photovoltaic performance of DSSCs with different metal counter electrodes*

In this section the performance of cobalt based DSSCs with 7 different metals as counter electrode substrates are compared. Here a low temperature catalyst layer was employed as not all of the studied metals endure high temperature treatments. Additionally, the catalyst layer was selected so that it does not act as a protective coating (c.f. sputtered

Pt)⁸ in order to see the reactions between the metallic surface in contact with the electrolyte. Thus we selected the porous carbon gel catalyst layers.¹⁶ These layers also have the benefit that they are non-transparent and thus they simplify the optical analysis as there is no back reflection from the counter electrode substrate. The adhesion of the catalysts layer to the different metals appeared to be good: the electrodes could be bent with neither detachments nor any other visible changes to the catalyst layers. The comparison of cell performance should therefore reveal the actual differences in the electrical performance caused by the counter electrode substrate itself. The drawback of using carbon counter electrodes is that its time constant of the porous carbon electrodes is the same range as in the photoelectrodes. Thus these two components are overlapping in EIS measurements and they cannot be measured individually. This limits the degree how well the differences in the electrical performance can be analyzed. The overall stability is, however, the main focus of this work and this can be evaluated regardless of such limitations.

Figure 1 shows that there were significant variations in the photovoltaic characteristics of the cells due to the different counter electrode substrates. Among the studied metals, the best cell performances were reached with StS 304 (Figure 1). Quite similar results were also measured with Ti, Ni and the reference glass cells with carbon catalyst layer. Additionally StS 321 worked fairly well. All of the above mentioned metals resulted in similar fill factors (*FF*) of ~45 % (Figure 1). In contrast, Cu, Al and Zn reproducibly had much lower *FF*, on in the order of 25 % (Figure 1), and very low efficiency. The V_{OC} was low in these three cases and that cannot be explained by charge transfer limitations at the

counter electrode. Thus the decrease of V_{OC} suggests that there have been changes at the photoelectrode resulting from the Cu, Al, and Zn counter electrode materials and such changes might also contribute the low i_{SC} values. The variation in both i_{SC} and V_{OC} in the case of these three metals was exceptionally large.

In the case of Cu based counter electrodes, there were significant visible changes in the electrolyte color from pale yellow towards dark brown shortly after the cell was assembled. The color change implies that the Cu substrate reacted chemically with the cobalt electrolyte. The apparent chemical changes may have played a significant contribution to the very low i_{SC} and V_{OC} values seen in the initial measurements. Such visible changes were not seen in the case of the other counter electrodes.

Regarding the Al substrate, similarly low fill factors have previously been reported in the case of another alternative redox couple (tetramethylthiourea / tetramethylformaminium disulfide dication).²⁰ In contrast, in that same publication cells equipped with StS and FTO-glass counter electrode substrates worked well.²⁰ This implies that there may be a more general issue with using Al as a counter electrode. One hypothesis regarding the poor fill factor in the case of Al is that the metal oxide layer topping the electrode is hindering the charge transfer in the counter electrode. Al_2O_3 is an insulator which has been successfully used as a recombination blocking layer in the case of cobalt electrolyte.²¹ While on the photoelectrode side such a blocking layer has a positive effect to reduce dark current, at the counter electrode side the opposite effect is needed and the layer merely hinders charge transfer. Zn could have similar problems. While this problem

should not be that large with ZnO as its band gap is not as wide as in the case of Al₂O₃, nevertheless it may still be too large. Alternative and/or additional factor could be the chemical instability of the Al and Zn electrodes, which is investigated in Sections 3.2 and 3.3.

Here the overall efficiencies were lower compared to some recent publications with record efficiencies with cobalt electrolyte.¹⁰⁻¹² This is mainly because we selected materials that have been stable in the case of iodine electrolyte but are known to reduce the performance e.g. methoxypropionitrile instead of acetonitrile as well as the dye (TG6), which has been reported to be relatively stable in with water based electrolytes.²² Furthermore, a larger cell size due to larger active area and the added window area to detect changes in the surface of the substrate and in the electrolyte color increases fill factor losses. All of these choices result in significant overall losses in the efficiency but improve the analysis of stability which is the main focus of this work.

The carbon gel was not the most efficient catalyst for cobalt even though it was very convenient here from other perspectives. This is shown by the fact that the reference cells on FTO glass with Pt give better performance than those with carbon gel (Figure 1). In Section 3.4, 5 different types of catalyst layers are tested on a metallic substrate.

3.2. *Stability of metallic electrode*

The stability of the metallic electrodes was investigated in the complete cells under actual operational conditions to evaluate the suitability directly. When using this strategy, other

instabilities affect the overall stability of the cell and those need to be taken into account in the analysis. With suitable reference cells the different mechanisms can still be separated. The focus of this study is to determine the stability of different metals in cobalt based electrolyte.

Figure 2 indicates that the efficiency of the glass cells with iodine electrolyte (denoted with glass Pt I in Figure 2) remains stable although there are some fluctuations in the individual parameters. This shows that the general preparation was done well and the major factor affecting the instability of the other cells was related to either the cobalt electrolyte and/or the counter electrode. Furthermore, when using cobalt electrolyte, the stability of the glass cells with carbon catalyst (Glass REF, Figure 2) does not differ from those with thermally platinized Pt catalyst layers (Glass Pt, Figure 2) which are generally regarded very stable. Finally regarding the metal cells, the cells based on both types of StS, Ni and Ti have a very similar aging response to that of the glass reference cells with the cobalt electrolyte (Figure 2). This suggests that these metals were as stable as the FTO glass in the cobalt electrolyte.

The stability of the Zn, Al and Cu cells is poor compared to the other cells (Figure 2). From the beginning, these cells had very low efficiency (Figure 1) and they only degraded further during the aging studies (Figure 2). The Al based cells additionally suffered from leakages during the aging study. The problem appeared to be related to softness of Al foils and their tendency to peel away quite easily; it may be possible to prevent such leakages by using a thicker Al to make the counter electrode sturdier or by

laminating the cell to give it more support. The instability of Cu cells was to be expected based on the fact that there were also visible changes in the cell as mentioned in the earlier section.

Although not all metals were stable in the cobalt electrolyte, it can be said that the cobalt electrolyte was in fact less aggressive than the iodine ones (relative to the reference cells on glass): In our recent study a cell with StS 304 as the counter electrode substrate degraded fully within 24 hours with an iodine based electrolyte,⁸ whereas here it was as stable as the glass for the entire study period (500 h). Literature also shows that Cu degrades in the iodine electrolyte in a few seconds (the electrolyte changes color as it is being filled to the cells)⁵ whereas here with cobalt it took longer (tens of minutes) for the visible changes to appear.

The instability of the reference glass cells with the cobalt electrolyte is a significant issue based on this study (Figure 2); while the iodine based glass cell degraded only about 5 %, the cobalt based glass cell degraded more than 50 %. The efficiency in the cobalt cells with glass, StS 304, StS 321, Ni and Ti varied a lot with time and those changes are dominantly due to the variation in i_{sc} . There was initially some increase in the performance in the cobalt cells and such improvement occurs often also in the case of iodine based cells, but generally not in that large extent. The reasons for the initial improvement for iodine based cells have not studied in literature but they are generally thought to be related to the electrolyte and the photoelectrode finding a steady state. It can be that there is something similar occurring in the cobalt cells as well. After the

initial improvement, the overall phenomenon is steady degradation. According to visual observations, there was desorption that was qualitatively consistent with the loss of i_{SC} . The electrolyte became reddish colored and the dyed TiO₂ layer turned pale during the aging process. In addition to the cells with the TG6 dye, some cells with the Z907 dye were made as well. The Z907 dye has given excellent stability results with iodine based electrolytes.²² However, here the Z907 dye suffered from similar stability problems (i.e. a significant loss of performance and a visible desorption of the dye) as the ones with the TG6 dye in the cobalt electrolyte (data not shown). Further studies are needed to find a solution for this instability at the electrolyte/dye interface, but that is out of the scope of this study as the main question here is the stability at the counter electrode/electrolyte interface.

3.3. *SEM analysis of the aged cells*

After the aging tests, the cells were subjected to SEM analysis to identify any changes. Here we compared the metal surface that had been in contact with the electrolyte (i.e. the active area) with a reference area outside the cell. Additionally, the glass based photoelectrodes were also examined to determine if there are for instance apparent corrosion products.

The Cu surface that was exposed to the electrolyte (Figure 3a) is clearly different compared to the area that was protected by the frame foil (Figure 3b). The basic difference is pitting on the aged Cu surface. The largest pits have a diameter about 1 μm and they are a clear sign of corrosion. Further concrete evidence of degradation was

found at the glass based photoelectrode taken from the Cu cell: The SEM images revealed formation of large particle clusters at the photoelectrode (Figure 3c). The elemental analysis indicated that the clusters at the photoelectrode were indeed mostly consisted of Cu. These Cu based particles transported to the photoelectrode are by-products of the degraded Cu counter electrode.

In the case of Zn, there were also some changes on the surface of the metal: namely formation of small corrosion pit holes on the grain boundaries (Figure 3d). Corrosion often begins from imperfections and defects of the metal and grain boundaries are one of the areas that corrode easily. Besides the intergranular corrosion, Zn containing particles (i.e. apparent corrosion products) were found in large quantities on the glass based photoelectrode similar to the case of Cu. Therefore it is clear that also Zn suffered from corrosion.

There were no visible changes on the surface of the Al substrate. There were, however, again significant amount of Al containing particles at the photoelectrode which indicates that the Al films had also suffered from corrosion. It appears that in the case of Al, the corrosion was so called “general/uniform corrosion” in which the metal corrodes evenly (i.e. no specific corrosion marks such as pit holes) and therefore it is hard to detect by investigation of the surface of the metal.

In contrast to Cu, Zn and Al, the other metals (StS 304, StS 321, Ni and Ti) did not show any visible changes on the metal counter electrode nor formation of particles containing

the respective metals at the photoelectrode as listed in Table 3. Thus StS 304, StS 321, Ni and Ti did not apparently corrode in the cobalt electrolyte. This conclusion is in good correspondence with the aging data of electrical performance (Section 3.2) which showed similar aging pattern for these 4 metals as for the reference glass cells in which case there were inherently no corrosion.

The apparent corrosion in the case of Cu, Zn and Al with the cobalt electrolyte could also explain or at least contribute to the poor initial performance. At least in the case of Cu, the corrosion reaction was seen to progress quickly and thus even the initial measurements were likely affected by the corrosion.

Table 3. Findings and analysis based on the SEM and EDS studies on the aged DSCs.

Substrate	Corrosion marks on metal CE	Corrosion products on glass PE	Conclusion
Cu	YES	YES	pitting corrosion
Zn	YES	YES	grain boundary corrosion
Al	NO	YES	general corrosion
Ni	NO	NO	no corrosion
StS 304	NO	NO	no corrosion
StS 321	NO	NO	no corrosion
Ti	NO	NO	no corrosion

3.4. Comparison of different catalysts

Both the initial performance characteristics as well as stability were as good in the case of StS 304 as with the reference glass cells. Furthermore when taking into account the cost factor, StS 304 seems to be best option among the studied metals. Here the next task is to compare the behavior of different catalysts on StS 304 and the reference glass. For this investigation Z907 dye was applied instead of the TG6 dye and also TiO₂ spray under layer was added. These changes have resulted in overall improvements in the performance of the cells compared the results presented in Section 3.1. This is in agreement with the literature where the Z907 dye was reported to work well with the cobalt electrolyte [24].

Table 4. The best performances with the different counter electrodes. HT = high temperature.

CE Substrate	Catalyst	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
StS 304	Carbon gel	3.7	0.639	0.47	1.1
	Chemical Pt	6.4	0.694	0.43	1.9
	HT Pt	5.9	0.693	0.37	1.5
	PEDOT-TsO	5.8	0.677	0.21	0.8
	PEDOT-PSS	4.6	0.687	0.15	0.5
FTO glass	Carbon gel	5.0	0.650	0.58	1.9
	HT Pt	5.9	0.691	0.69	2.8
	PEDOT-TsO	6.1	0.687	0.46	2.0
	PEDOT-PSS	5.5	0.663	0.37	1.3
Iodine reference FTO glass	HT Pt	8.1	0.781	0.65	4.1

The best results with the StS 304 based CE were reached with a low temperature chemical platinization leaving the thermal platinization as second best (Table 4). In

previous studies with StS based electrodes in iodine electrolyte, the low temperature treatments have resulted in a higher catalytic activity compared to thermal platinization in contrast to the case of glass based electrodes.^{4,8} This feature is assumed to be a result of higher contact resistance between the metal and the catalyst layer caused by the growth of an oxide layer between them in the heat treatment. Unrelated to the actual electrocatalytic activity of the catalyst particles themselves, this would affect both cobalt and iodide based cells, as found in the experiments.

In the case of StS 304 based electrodes with carbon gel, the i_{sc} is low resulting in a low efficiency (Table 4). The lower i_{sc} compared to the other cells is understandable as the counter electrodes with the other catalyst materials can cause back reflection while the carbon gel electrode does not. Here, as the photoelectrodes were non-scattering and quite thin, the effect of light reflection is likely to be significant. The cell with carbon gel based StS 304 counter electrode, however, has a relatively good FF (Table 4). With a low i_{sc} , it is, however, easier to get a higher FF , but when taking that into account it is still much better option than the polymer catalysts.

Interestingly, PEDOT-TsO and PEDOT-PSS catalysts did not work well on metal counter electrodes, the fill factor was particularly poor in the case of PEDOT-PSS (only 15 %, Table 4). The problem was so serious with both PEDOT layers that the charge transfer at the counter electrode was actually limiting i_{sc} . Both of these polymer catalysts worked much better on FTO-glass resulting in over 2-times higher FF and efficiency compared to the same catalysts on StS 304 (Table 4). Recently very high efficiencies were reported

with PEDOT polymer catalyst on FTO-glass and they were found to work much better compared to platinum catalyst layer.¹² The PEDOT layers used here did not give as good results as in literature.¹² The reason might be related to the differences in the materials (e.g. the PEDOT also contained gold particles in the other study)¹². However, the main point we have demonstrated is that these polymer catalyst layers were clearly unsuitable for use on StS.

4. Conclusions

The purpose of this work was to investigate the possibilities of using different metals with cobalt electrolyte in dye sensitized solar cells. It was noted all the studied metals require a separate catalyst layer to be used as efficient counter electrodes. The studied metals with a porous carbon catalyst layer can be divided into two main groups: Firstly, StS 304, StS 321, Ni and Ti gave similar performance and stability compared to the reference glass based cells. Secondly in contrast, Cu, Al, and Zn showed both poor initial performance and poor stability. The SEM analysis revealed clear marks of corrosion for Cu, Zn and Al: Cu and Zn had changes in the structure of the metallic surface and in all three metals clear corrosion by-products were found at the glass based photoelectrodes. The chemical instabilities may even have affected the initial performance.

A significant challenge for the future studies is the improvement of the overall stability of the cells with cobalt electrolyte. There is clearly degradation at the electrolyte / dye interface that is detrimental to the cell performance. This instability was the factor

limiting the lifetime of glass based cells as well as those metal based cells that did not suffer from corrosion.

Among the studied metals, StS 304 showed the most potential in terms of efficiency, stability and cost. The testing of 5 different types of catalyst layers on StS 304 revealed that low temperature platinization worked better compared to thermal platinization and resulted in the highest efficiency. Furthermore, carbon catalyst layer on StS gave quite good charge transfer at the counter electrode whereas both PEDOT-TsO and PEDOT-PSS were clearly unsuitable on StS 304 even though PEDOT-TsO worked well on FTO glass.

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Figure captions

Figure 1. Average a) i_{SC} , b) V_{OC} , c) FF and d) efficiency (η) of cells with the different substrates at the counter electrode. The error bars show the standard deviation. Notation “glass” refers to FTO glass. The counter electrodes used a carbon catalyst layer except for reference cells marked with Pt which used a platinum layer. The cells had cobalt electrolyte except for the Glass Pt I cells which was made for comparison with the iodine containing electrolyte.

Figure 2. Normalized aging data (i.e. the aging data divided by initial performance data for each cell) in light soaking 1 Sun at 40 °C. The cells are kept in open circuit during the light soaking. Notation “glass” refers to FTO glass

Figure 3. SEM images of the Cu electrode which a) has been subjected to the electrolyte whereas b) has not. c) Photoelectrode of the cell with Cu based counter electrode shows the presence of Cu containing particle cluster formation (one such particle is pointed with the red arrow). d) Surface of the Zn electrode after aging shows pit holes at grain boundaries (pointed with the red arrow).

Figure 1

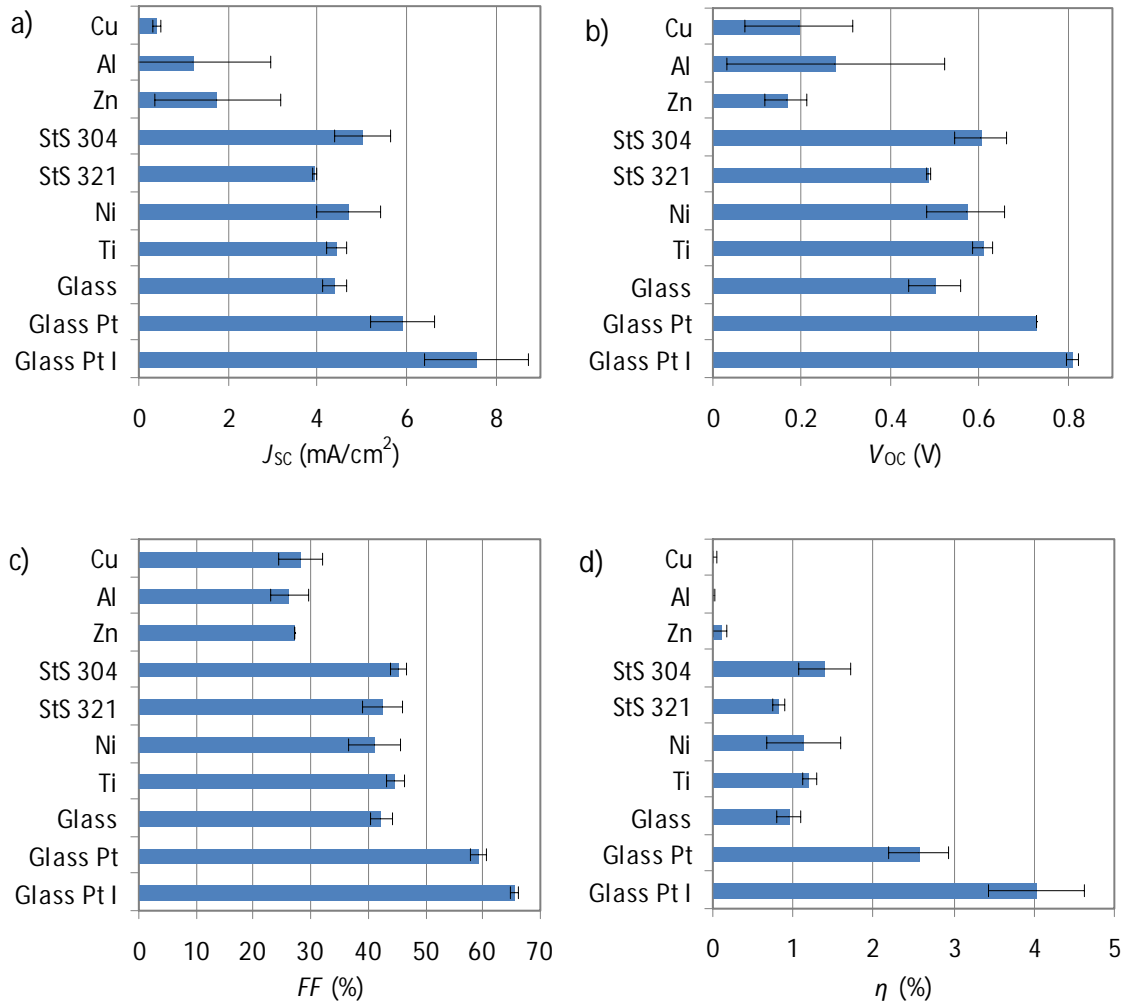


Figure 2.

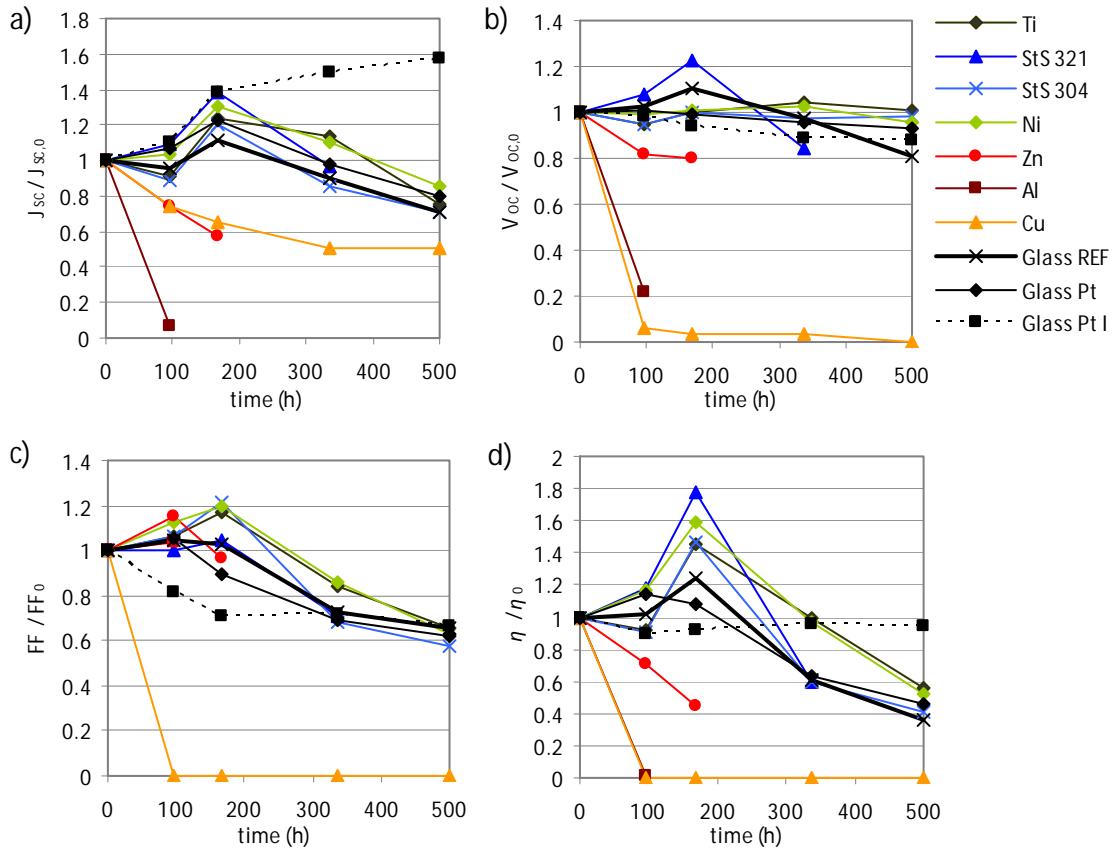


Figure 3.

