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# Insights into corrosion in dye solar cells

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## Abstract

The main issue in using low cost metals in dye solar cells is the corrosion caused by the liquid electrolyte. Contrary to typical applications of metals, the adverse effects of corrosion in dye solar cells are related to irreversible depletion of charge carriers from the electrolyte rather than consumption of the metal itself. It is calculated that the penetration rate due to corrosion should not exceed  $10^{-4}$  mpy (a couple of nanometers per year) to ensure device lifetime longer than one year. This is 10000 times slower rate than what is considered to be a general benchmark value for very low corrosion rate in the field of corrosion science, and has a major effect on how corrosion should be investigated in the case of dye solar cells. Different methods, their applicability and limitations to investigate corrosion in dye solar cells are evaluated here. The issue with most techniques is that they can detect metals that are clearly corroding, but they have significant limitations in proving a metal stable. Our investigation shows that the most reliable information on corrosion is obtained from complete dye solar cells that are exposed to working conditions. A combination of color analysis of the electrolyte to such measurement is proposed as a means to extrapolate future performance of the cells and estimate potential lifetimes of the dye solar cells in regards to corrosion.

**Keywords:** Metal; Stability; Redox couple; Corrosion; Dye-sensitized

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# 1. Introduction

Dye sensitized solar cells, also known as dye solar cells (DSC), have a potential for easy manufacturing and low cost [1-3]. Production of DSCs on flexible substrates such as metals is an interesting option and it has also been chosen for commercial DSCs [3,4]. Metal foils have superior conductivity compared to transparent conductive oxide coated glass substrates [5] and they can be also significantly cheaper [3]. As thin foils they are flexible and thus lend themselves to roll-to-roll production, which is important in reducing manufacturing costs [2,3]. Metal based DSCs (Figure 1) have reached 9.15% efficiency with stainless steel based counter electrodes [6] and 8.6% with stainless steel based photoelectrodes [7].

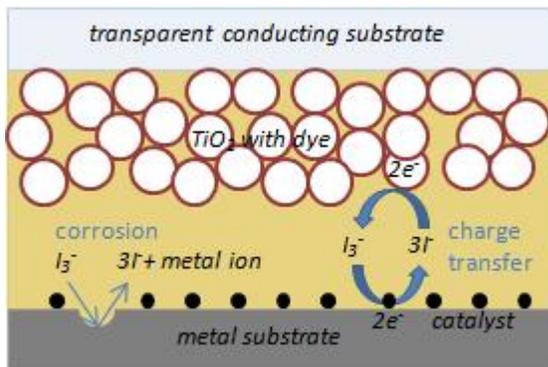
The critical question related to use of metals as a conducting substrates in DSCs is their propensity to corrode when exposed to the conventional iodine based electrolyte in DSC [4]. For instance no counter electrode based on stainless steel has been reported to be stable in long term aging studies using conventional iodine electrolyte without a separate corrosion blocking layer [4]. Therefore, to make an intrinsically stable dye solar cell with a metallic electrode, the application of highly corrosion resistant and expensive metals such as titanium have been suggested [8]. Our recent studies have also shown that the corrosion problem is not limited to the conventional iodine electrolytes, but is also an issue with alternatives such as electrolytes based on cobalt complex redox couple [9].

In this contribution, experimental methods typically used in corrosion science for determining corrosion rates of metals are evaluated from the point-of-view of their applicability for studying corrosion of metal substrates in DSCs. Several different methods have been used in the literature for investigating corrosion in dye solar cells, but their measurement sensitivity and accuracy has not been contrasted with the corrosion rate values that would be considered low enough for DSC application, leaving it somewhat unclear what type of conclusions each method can provide.

In this contribution we first define the maximum corrosion rate that could be tolerated in the DSC while still considering it to be stable enough for commercial applications. The different methods to investigate corrosion are then reviewed and their corrosion rate measurement sensitivity is contrasted with the maximum acceptable rate. In the case of electrochemical corrosion polarization measurements new experimental results are reported that complement the review with data that were not available in the literature. The different methods are compared and their limitations are discussed. The methods are classified to those that are sensitive enough to conclude a metal stable, and to those whose sensitivity is not enough to confirming stability but only instability, in a given electrolyte solution.

It turns out from our analysis that in the case of DSC the scenarios for corrosion are very different compared to a typical case in the field of corrosion science where the main concern is damage on the metal and its surface: since the corrosion induced degradation of DSCs occurs mainly via depletion of charge carriers in the electrolyte due to their consumption in the corrosion reaction, corrosion studies of DSC require measurement techniques that are sensitive to changes in the electrolyte - not only in the metal.

Variety of different methods is analyzed here: Firstly, we look into the applicability of readymade tables of Standard Electrochemical Potentials and Pourbaix diagrams in understanding corrosion in dye solar cells. Secondly, the different methods to investigate spontaneous corrosion are reviewed. Those methods are based on soaking the metal in electrolyte and the corrosion is observed by change in color, weight, chemical composition, or resistance. Thirdly, corrosion polarization measurements are investigated and measurements are made to in order to analyze the method. Fourthly, analysis of corrosion in complete dye solar cells is discussed. This includes changes in performance and electrolyte color as well as microscopic changes in the surface of the metal and elsewhere in the cell.



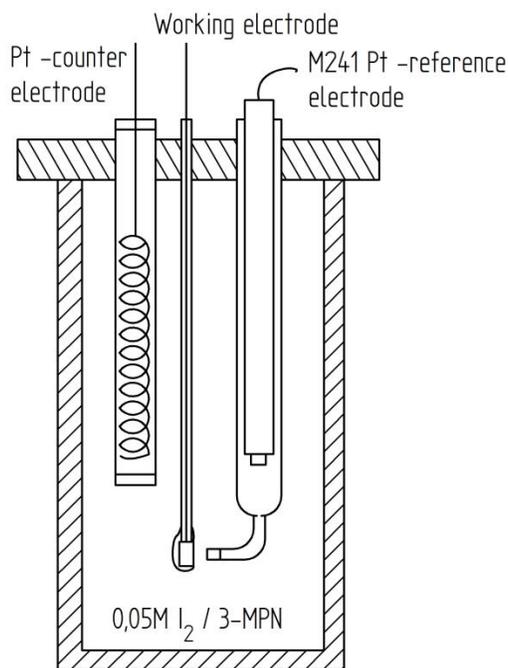
**Figure 1. Schematic illustration of a dye solar cell with metal as the counter electrode substrate. Figure also illustrates normal charge transfer reaction in the electrolyte and corrosion of metal by the conventional  $I_3^- / I^-$  electrolyte.**

## 2. Experimental methods

To investigate corrosion polarization measurement, experiments were carried out here since no sufficient data was found in the literature for a complete analysis. In these measurements, stainless steels (StS) 304 and 316 were used as samples. The metals were laser-cut into circular pieces with a surface area of 0.27 cm<sup>2</sup>, and their surfaces ground to a constant roughness using P800 silicon carbide abrasives and ethanol. The samples were then washed in both acetone (Fluka ≥ 99.5%) and technical ethanol in ultrasonic bath for 10 minutes. Next, a stainless steel wire was welded to the sample using a capacitor-discharge welder (Heatmasters HM190<sup>®</sup>). The quality of the weld was monitored by measuring the resistance across the weld using a multimeter. To model typical surface conditions, prepared samples were exposed to ambient laboratory environment for 48 hours before measurements were conducted. The indium tin-oxide coated polyethylene terephthalate (ITO-PET) sheets were used as non-corroding reference and they were cut into the same circular sample size by hand with the exception of the connecting steel wire being replaced with a narrow ITO-PET sheet painted with silver conductive paint (Electrolube<sup>®</sup>). Each of the samples were then sealed into 2.5 mm diameter glass tube sample holders using a polymer hot melt adhesive that aimed to insulate and control the exposed effective surface area of the sample (Figure 2). Due to possible adhesive additive solubility into the 3-methoxypropionitrile (3-MPN), which is the solvent of the electrolyte, a gentle

stirring motion was applied into the cell to prevent substance accumulation in proximity to the sample surface.

The corrosion resistances of the samples were evaluated by conducting cyclic potentiodynamic polarization measurements using a Gamry Instruments G750 Potentiostat<sup>®</sup>. The conventional three-electrode glass cell (as detailed in Figure 2) was used to perform the tests. A platinum M241Pt (Radiometer analytical<sup>®</sup>) reference electrode in a saturated KCl(aq) (Radiometer analytical<sup>®</sup>) environment separated from the electrolyte by a 40-100 Å porous membrane (Vycor<sup>®</sup>) was used instead of a SCE due to salt incompatibility. Another spiral-shaped platinum counter electrode was used as the counter electrode. The electrolyte solution used in the corrosion polarization test was a very simplified one, a 50 mmol I<sub>2</sub> (Rectapur ≥ 99.0%) in 3-MPN (Aldrich ≥ 98.0%). The samples were placed in the cell and immersed in the electrolyte for 5 minutes prior to measurements to stabilize the steady state potential. The potentiodynamic polarization test was conducted from -0.1 V to 0.5 V vs. the steady state potential of each sample with a scan rate of 1 mV/s [10]. The resulting data was depicted as Tafel plots from which the relative corrosion current densities and corrosion potentials can be determined.



**Figure 2. Schematic illustration of the measurement setup in the corrosion polarization measurements.**

### 3. Results and discussion

Before going into detail of the corrosion analysis, it is important to look into the general scenario of corrosion in dye solar cells. This gives guidelines on how to approach the question of how resistant the metals should be towards corrosion and what rate of corrosion is good enough for practical applications. Typically, the main issue in corrosion is how the metal is consumed in the

corrosion reaction in a way that makes it mechanically unstable, for instance it breaks under pressure or there is a hole. On the contrary in dye solar cells, the performance failure caused by corrosion of the metal substrate occurs due to corrosion induced chemical changes in the electrolyte rather than in the metal: the primary failure mode of DSCs with metallic counter electrode has been loss of short-circuit current density due to loss of tri-iodide in the electrolyte, as evidenced by simultaneous loss of electrolyte color [11,12]. The mechanical stability of the metal has been practically unaffected and there were typically only few marks of corrosion on the surface in SEM analysis [11,12].

The consumption of the corrosive ions in the electrolyte decreases the maximum current that the electrolyte can carry, which is also known as the limiting current  $I_{lim}$ . When  $I_{lim}$  decreases, at some point it starts to limit the short-circuit current density  $I_{SC}$ . Typically the corroded cell has lost all tri-iodide and thus there is no practical  $I_{lim}$  and therefore both  $I_{SC}$  and efficiency  $\eta$  go to zero [11,12]. Whilst the loss of charge carriers is the ultimate cause for cell degradation, there are also other effects on performance due to corrosion. First, if the surface is consumed, the amount of catalyst in connection to the metal substrate reduces, which makes the charge transfer sluggish and the fill factor  $FF$  decreases [11]. Second, the products of corrosion of the counter electrode, such as metal cations dissolved in the electrolyte, have been seen to end up at the photoelectrode where they may increase current leakage at the photoelectrode and thus decrease the open circuit voltage  $V_{oc}$  [11]. Although the previous example described the corrosion in the case of iodine electrolyte, similar effects have also been seen with alternative electrolytes such as cobalt complex electrolyte [9].

### 3.1 Penetration rate of corrosion

As discussed above, the loss of performance in the cell appears to be dominantly due to the loss of  $I_{SC}$  [11,12]. The most examined metal in the corrosion studies is stainless steel [4,5,9,11-15], which is thus selected as the material for these examples. Typical stainless steel (StS), such as grade 304, also known as standard stainless steel 18/8, has the nominal composition of approximately 70 % Fe, 18 % Cr and 8 % Ni. The cell is fully degraded when all the tri-iodide in the electrolyte is consumed. Next it is calculated how deep the usual amount of iodine in a typical cell geometry can corrode the metal if uniform penetration is assumed. To simplify the analysis, the calculations are done for Fe only. The error due to this simplification is less than 1 % as the molar densities of all other main components of StS are quite similar. Typically the iodine concentration (converting to tri-iodide) in the electrolyte is about 0.05 M and the thickness of the cell 20  $\mu\text{m}$ . This means the amount of iodine per surface area is  $1 \cdot 10^{-5} \text{ mol/dm}^2$  ( $=1 \cdot 10^{-3} \text{ mol/cm}^2 = 1 \text{ mmol/cm}^2$ ). The corrosion reaction of iron is a two electron reaction [16] such as that of Zn and the corrosion reactions of Zn in typical dye solar cell electrolyte are described in detail by Toivola et al. [13]. Based on those it can be deduced that corrosion of iron in tri-iodide is the following:



In the case of iron (density 7.850  $\text{g/cm}^3$  and molar mass 55.84  $\text{g/mol}$  [16]), it can be derived that the typical amount of iodine in the cell could consume about 7 nm uniformly from the surface of

the metal.

The very thin metal sheets that suit the best preparation of these devices are 50  $\mu\text{m}$  [11] so the maximum uniform corrosion (i.e. all corrosive ions consumed) would only take away about 0.01 % of the metal. This further clarifies that the problem is indeed *not* in the loss of metal or its integrity but in the loss of corrosive ions.

This consumption of metal can be translated to a penetration rate (given as mpy, 1 mpy = 25.4  $\mu\text{m}$  per year) when taking into account the timeframe of the process and assuming constant rate for the process. It seems quite likely that shorter lifetimes than 1 year for 100 % degradation would not have any commercial value and the corresponding penetration rate is about  $3 \cdot 10^{-4}$  mpy. So as a rule of thumb, the penetration rate should not exceed  $10^{-4}$  mpy in any case. Many commercial applications would require longer lifetime and for instance conventional silicon solar cells guarantee 90 % stability (i.e. 10 % degradation) for 20 years. In the case of 10 % loss in 20 years, the maximum acceptable rate of corrosion would be  $10^{-5}$  mpy. In this calculation it was taken into account that 0.05 M  $\text{I}_2$  provides 200 % excess of tri-iodide [17] compared to what is required to transfer  $I_{\text{SC}}$ . It was assumed the performance loss is seen only when  $I_{\text{lim}}$  goes below  $I_{\text{SC}}$  and from there on the loss of performance is directly proportional to loss of  $I_{\text{SC}}$ . There are some changes in the other parameters as well, but focusing on the current is a working approximation based on previous results [11,12,17].

Generally in corrosion studies (not in dye solar cells), penetration rates less than 1 mpy are “considered to be excellent to outstanding” [10]. The acceptable rate depends on the engineering application, but to this is a good rule of thumb for a large number of applications. If the rate of corrosion is 1 mpy in dye solar cells, it would mean that the whole device would be completely degraded in about 2.5 hours, which would be extremely poor stability. In other words, more than 10000-times better corrosion resistance is required in dye solar cells compared to what is generally regarded as excellent. This gives a good impression of how demanding the situation is in the case of dye solar cells.

The calculations were done here for iron/stainless steel, but the results are on the same range for other metals as well. For instance aluminum, which has one of the biggest differences in molar density [16] among the typically applied metals, has only 30 % difference in the corrosion rate. The extremely demanding corrosion resistivity is a likely factor to why even the alternative electrolytes, that had been assumed to be non-corrosive, corroded some metals [9]. In the case of cobalt complex electrolyte, several studied materials (copper, zinc and aluminum) corroded in a few days [9]. To confirm this deduction, we applied another alternative electrolyte with metal substrates, namely electrolyte with ferrocene/ferrocenium redox couple prepared as described in literature [18]. In our tests also this electrolyte showed clear marks of corrosion. For instance, in the case of copper substrates both the metal surface and the electrolyte changed color overnight in dark conditions. Since the limit for sufficient corrosion stability is so high for DSCs, this further emphasizes why corrosion measurements need to be conducted as well for alternative electrolytes that are generally regarded as non-corrosive.

### 3.2 Progression of corrosion in metals by the electrolyte

In the above analysis, corrosion was assumed to progress with a constant rate and to consume the metal evenly. Here the validity of this assumption for different metals is evaluated.

In the investigation by Reynolds et al. corrosion was examined based on optical absorbance data which is directly proportional to amount of iodine in the cell [15]. The amount of iodine is again inversely proportional to corrosion [15] and, if the reaction progresses linearly, the rate of corrosion is constant. Here linear fits were applied to that set of data [15] and it showed that for instance 99.0% pure Aluminum had excellent linearity (goodness of fit  $R^2$  value 0.998) and verified that there was a constant rate of corrosion in that particular case. With some other materials (99.9% Al and 99.9% Mo), the linear fit was also reasonably good ( $R^2$  value  $\sim 0.87$ ) and a constant rate progression is in their cases acceptable.

In contrast to those results, iron was shown to be stable for some time but then degraded rapidly [15], i.e. there was a so-called incubation time during which no corrosion occurs. In that case the assumption of a constant rate for the corrosion does not appear as a valid one. In general, it has been noticed that alloyed metals tend to have an incubation period and the corrosion is often localized [10]. For instance in stainless steel, the corrosion protection is based on Cr and the corrosion starts from areas with a lower Cr content [19]. In aging experiments of DSCs, this has been shown as there has been pitting corrosion occurring locally [11]. In contrast, when the metal is dominantly of only one metal, the corrosion progresses typically more uniformly (i.e. general corrosion) [10]. For example Al substrate was shown to corrode in cobalt electrolyte namely by general corrosion [9].

Even though corrosion may not progress with a constant rate with all the metals, it is used here as the working estimation to get an idea of approximate rate of the corrosion reaction. The focus in this contribution is on orders of magnitude when looking at the rate of corrosion and the simplification made here should be adequate for this purpose. It is, however, good to keep in mind that the constant rate approximation may not be sufficient for very detailed predictions.

### 3.3 Spontaneous corrosion and corrosion potential

In the case of iodine electrolyte, many metals have been shown to corrode when merely in contact with the electrolyte i.e. with no applied energy from an external source or from the photovoltaic reaction. Corrosion where no external energy is required is called spontaneous corrosion. These thermodynamic reactions have a negative Gibbs free energy.

In the case of aqueous solution, there are lists of Standard Electrochemical Potentials that can be used to predict potentials where materials are thermodynamically stable, but it needs to be carefully considered when this can be applied. These tables give the potential when net dissolution is impossible in a case where having a metal (solid) is in 1 M aqueous solution of its salt [10]. This definition is important to remember when evaluating its applications. First, the solution in the case of dye solar cells is not typically aqueous. Second, the solution does not contain a salt of the metal, but other salts. Because of the differences in the setup, such general

tables cannot be applied directly to predict which metals will corrode spontaneously in the electrolytes.

Comparing standard potential tables with actual dye solar cell measurements shows that the tables cannot be used to predict reactions in dye solar cells: the standard potential tables would predict that Ti would be thermodynamically unstable as its potential (-1.63 V vs. NHE [16]) is more negative compared to electrolyte redox potential (+0.4 V vs. NHE [20]). In practice, Ti has been found to be one of the few metals that are stable in iodine [11,15]. On the other hand, Ag is “predicted” to be thermodynamically stable when extrapolating such tables (+0.799 V vs. NHE [16]), but in reality it corrodes very quickly when in contact with the electrolyte. In fact, the protection of the silver current collector contacts from corrosion by the electrolyte is one key issue in the large area dye solar cells [21]. In conclusion, it can be said that the standard electrochemical potentials cannot be extended to predict which metals will spontaneously corrode in dye solar cells. If the steady state potential for corrosion reaction (i.e. corrosion potential) is examined, it should be measured with each electrolyte separately.

Another type of analysis that gives the potential where metals corrode are Pourbaix diagrams. Pourbaix diagrams give graphical representation on which pH and potential region metals are stable and when they corrode. They are often used in the analysis of corrosion when the solution is more complicated than pure water [10] (c.f. Standard Electrochemical Potential tables for pure aqueous solution). However, the fact that there is pH involved tells that the analysis is made in aqueous solution as pH cannot be defined in any other solution. For non-aqueous solutions, there are alternative diagrams to Pourbaix diagrams that could be made [22,23]. There are, however, no readily made diagrams that could be applied directly for electrolytes in dye solar cells since those are very rare in corrosion studies. Even if there were such diagrams that described materials relevant to dye solar cells, the interpretation of sufficient stability for this particular application might not be reliable as the definition of good corrosion resistance is so far beyond the common standards (cf. Section 3.1).

Here we come again to the important point that the electrochemical standard potentials and Pourbaix diagrams do not reflect corrosion current which is related to the corrosion rate. Thus, looking only at the corrosion potential it can be determined which reaction is thermodynamically possible, but not how fast the reaction would be. The rate of the corrosion reaction is, however, highly important when thinking of practical applications and their lifetimes as was discussed in the previous section. Hence, other types of investigations of corrosion are that also give indication on timeframe of the corrosion reactions are perhaps more useful.

### 3.4 Spontaneous corrosion and electrolyte soaking tests

Next we evaluate the conventional corrosion tests that examine spontaneous corrosion. Quite often the spontaneous corrosion of metals is investigated by placing the metal in electrolyte solution (so-called electrolyte soaking test, Figure 3) and 1) by observing the weight loss of the metal [24], 2) the change of electrolyte color [5,13-15], 3) the amount of dissolved metal in the electrolyte [5,13,14], or change in catalytic activity of the substrate [25].

First we consider the method of observing corrosion by studying the changes in weight of the metal. If there is a 7 nm loss in the thickness of the substrate, which corresponds to the complete destruction of a dye solar cell, it would result in a weight loss of only  $5 \mu\text{g}/\text{cm}^2$ . Typically electrolyte soaking tests are not very long (weeks or months [5,13-15,24], not years) and in this case the acceptable loss in the weight need to be scaled down accordingly which makes the determination of sufficiently stable metals even more difficult. There are scales that would go low enough, but the varying amount of minor impurities (for instance adsorbed moisture from the air) on metal from one measurement time to another could easily dominated the response. On the other hand, if there is a clear changes in the weight of the metal, the corrosion resistivity can be deemed too low for dye solar cells. In the literature weight loss has been investigated in the range of  $\text{mg}/\text{cm}^2$  [24] (i.e. 1000-times higher that required for sufficient stability) and, if corrosion is seen in that high a rate in some metal, it is sure that the metal is not stable enough and can e.g. be exempt from further study of possibly suitable materials. However, in the opposite case it can be difficult to confirm with this method that the corrosion resistance of a metal is good enough.

In an electrolyte soaking test the metal (about  $1 \text{ cm}^2$ ) is typically immersed in about 1-10 mL of electrolyte solution (Figure 3) [13]. The amount of electrolyte in dye solar cell is about  $2 \mu\text{L}$  so there is a very high excess of electrolyte in this kind of corrosion test compared to normal cell configuration. Thus if  $2 \mu\text{L}$  of electrolyte degraded (full degradation of real solar cell), it would mean a 0.2-2 parts per thousand difference in the soaking electrolyte solution and there would thus be no significant change e.g. in the electrolyte color. So the conclusion is the same as previously: if something can be detected with this method, the corrosion resistance is too low for dye solar cells but the opposite deduction cannot be confidently made.

Decreasing the amount of electrolyte in an electrolyte soaking test makes the detection of color change much easier. Thus encapsulating the electrolyte and the metal in a "cell type" configuration (Figure 4), i.e. having only the amount of electrolyte available for the corrosion that is present in a real cell, is a much better approach for detecting color changes [13,15]. If taking the 1 year and full loss of performance as a limit of sufficient stability, the loss of tri-iodide in one month long test should not exceed approximately 10 % and changes in that level can be easily detected optically [15,26]. For many applications such a short lifetime may not, however, be sufficient and e.g. 20 years and 10 % performance loss would require accuracy of 1 % in the optical measurements which is often below or bordering the measurement accuracy. This situation can be improved by increasing the measurement time accordingly to meet the accurate range of measurement.

Another method used in the corrosion studies has been the analysis of the electrolyte from the electrolyte soaking test. The amount of electrolyte in a solar cell is likely to be too small for such analysis so typically the solution from immersion tests has been used for this purpose. In such a test the limit for detecting residues of the metal has been  $0.2 \text{ mg}/\text{L}$  [13]. If the there was 10 mL of electrolyte solution in the soaking, it would mean that there should be a minimum of  $2 \mu\text{g}$  of metal residues in the electrolyte to get beyond the detection limit. It was above calculated that

the  $5 \mu\text{g}/\text{cm}^2$  is the minimum acceptable dissolution of metal in one year (100 % performance loss) so the measurement time needed to get to that kind of level would be about half a year. If requiring good corrosion resistivity (20 years, 10 % loss of performance), the required measurement time would be years. However, again this kind of measurement is useful in short time periods for detecting and ruling out candidate metals are definitely not suitable for dye solar cells.

Since the corrosion changes the surface of the metal and its catalytic properties, the progression of corrosion has also be investigated using electrochemical impedance spectroscopy (EIS) to evaluate changes in the resistance related to the catalytic reaction [25]. This method also suits well for comparison of tendency of the metals to corrode. However, it is not that clear how small a change in the catalytic properties would be related sufficient stability against corrosion. Perhaps such issues could be determined if the method was coupled with some other method such as optical analysis in cell-like configuration.

Based on the above comparison of different techniques, it appears that evaluating the color change in the encapsulated cell-like configuration is the most accurate and quickest way of investigating if a metal is sufficiently stable towards spontaneous corrosion.

The other issue, not assumed above, is that also the working conditions, in particular polarization, affects the corrosion rate [11,12] so the analysis needs to extend beyond spontaneous corrosion occurring at zero polarization. Our previous studies have shown that metals, that had been stable in electrolyte soaking tests made with cell like configuration, did corrode when they were used in actual working cells [11,12]. Therefore actually all tests listed in this section can only be used to determine which metals are clearly not sufficiently stable for complete dye solar cells (even if the spontaneous corrosion could have been measured accurately enough) and narrow down the list for further examination.



**Figure 3. Electrolyte soaking test done in two ways: On the left there is the conventional style setup with excess electrolyte and metal substrate is literally soaking in electrolyte. On the right, there is the “cell type” setup with reduced amount of electrolyte.**

### 3.5 Corrosion current density

A type of corrosion that appears to be important from the perspective of complete solar cells is electrochemical corrosion i.e. in which external energy in relation to the corrosion reaction is needed. In the case of dye solar cells, the external energy for the corrosion does not need to come outside the cell but rather the corrosion reaction can be powered (or prevented) by the energy provided by the photovoltaic reaction. The polarization is in some other applications used as a method to even prevent corrosion. As described earlier, some metals, that were stable in electrolyte soaking tests i.e. in zero polarization, even in cell-type encapsulated configuration with enhanced accuracy, suffered from corrosion in complete DSCs [11-13]. In operational conditions, the electrodes in the cells are polarized and that can have a significant effect on the corrosion reactions. This brings us to another important point related to polarization: the performance of solar cells is often measured in such a way that the cell is polarized by external potentiostat and actually the measurements themselves could in the worst case accelerate or even trigger corrosion reactions depending on the cell configuration and the potential. To avoid the measurements from causing corrosion, the polarization of the metal based cells in measurements beyond the IV range that the cell experiences in normal operational conditions should be avoided.

Generally polarization measurements are performed to investigate the corrosion rate at different potentials at the metal / solution interfaces and used to determine the safe region (if there is one) for the operation. The polarization measurements are based on Faraday's First Law that states "the mass,  $m$ , of an element at an electrode is directly proportional to the amount of electrical charge,  $Q$ , passed through the electrode" [10]. In the case of iron, the corrosion is a two electron reaction [16]:



The corrosion current density,  $i_{\text{corr}}$ , that corresponds to a specific penetration rate,  $p$  [mpy], can be derived from the following equation which is based on the Faraday's first law and the stoichiometry of the reaction [10]:

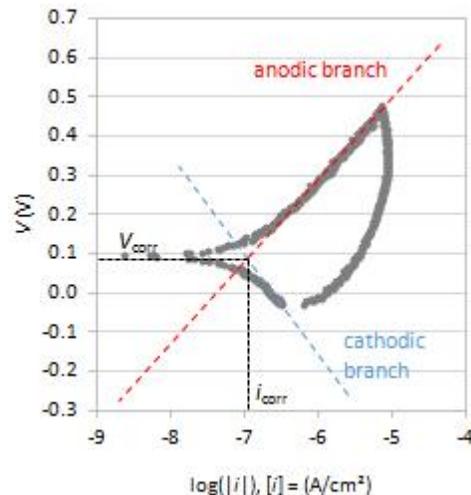
$$i_{\text{corr}} \left[ \frac{\text{mA}}{\text{cm}^2} \right] = \frac{npp}{129m_a} \quad (3)$$

where  $n$  is the number of electrons lost per oxidized atom,  $\rho$  density [ $\text{g}/\text{cm}^3$ ] and  $m_a$  is the atomic mass [g].

Following the previous example of corrosion of iron in iodine electrolyte in a typical dye solar cell configuration,  $i_{\text{corr}}$  corresponding to the penetration rate of  $3 \cdot 10^{-4}$  mpy is only 0.7 nA/cm<sup>2</sup>. This is an extremely low  $i_{\text{corr}}$  value as generally in corrosion science about 2  $\mu\text{A}/\text{cm}^2$  is the limit of excellent corrosion stability [10]. From practical point of view, it can be considered that  $i_{\text{corr}}$  should definitely be below 1 nA/cm<sup>2</sup> in the case of typical dye solar cells and it serves as a good rule of thumb for the analysis of the polarization measurements in Section 3.6.

### 3.6 Polarization measurements

Evans diagram can be used to determine the steady state corrosion (thermal equilibrium, no polarization) rate in  $i_{\text{corr}}$ . The value can be read from the point of IV-curve where Tafel extrapolations of the anodic and cathodic rates are equal (Figure 4). The same point defines the corrosion potential (Figure 4). Generally the Tafel extrapolation of the anodic branch is assumed to correspond to the corrosion reaction. From the Tafel extrapolation the potential that corresponds to the maximum allowed corrosion rate can in *theory* be determined. Furthermore predictions of corrosion rates can be obtained from the measured current in principle, which would allow prediction of lifetimes for the system. In the literature this method has been used by Fan et al. but only to rank in which order metals corroded [27]. Here we investigate in detail the possibilities and limitations of this technique.



**Figure 4. Example of Tafel plot illustrating the Tafel extrapolations for the anodic and cathodic branch as well as the corrosion current and potential.**

The major assumption in the polarization measurements is that all the measured current of the anodic branch is related to the corrosion reaction. At the counter electrode of a dye solar cell (Figure 1), there is the charge transfer from the counter electrode to iodine redox reaction (not corrosion of metal) which is the essential reaction for the operation of the device. Even without any kind of separate catalyst material, this “catalyst” reaction is present at the substrate / electrolyte interface, but the rate is significantly reduced. Thus the measured current at the metal / electrolyte interface is divided between those two reactions (catalytic performance and corrosion).

To make initial estimations of the significance of charge transfer at a substrate/electrolyte interface (without a catalyst) to corrosion polarization measurements, a substrate which does not corrode is investigated. In the case of bare FTO-glass substrate in which case there is no corrosion, the steady state current (0 V) related to catalytic activity from Tafel extrapolation is about  $10 \text{ nA}/\text{cm}^2$  [28]. That is problematically large compared to the range of sufficiently low corrosion reaction which was below  $1 \text{ nA}/\text{cm}^2$ . Therefore catalytic reaction may easily dominate the response if a normal electrolyte is used. The steady state current related to the catalytic

activity will vary between the different materials. However, already this shows that catalytic reaction cannot be assumed insignificant, but it needs to be carefully assessed.

The catalytic reaction needs to be suppressed to have the corrosion reaction to dominate the response. Here we tested a simplified version of the electrolyte: 0.05 M I<sub>2</sub> in 3-methoxypropionitrile i.e. just the corroding agent and the solvent. The idea of that was to suppress the current by leaving out the component providing the counter ion for redox reaction, such as LiI. However, even with this simplified electrolyte the steady state current was about 10 nA/cm<sup>2</sup> and hence the attempt to suppress the corrosion reaction failed.

To investigate the method and its applicability in detail, a corrosion polarization test was made. For this purpose three substrates were selected that are known to have different corrosion rates: StS 304, StS 316 and ITO-PET [11]. In these measurements ITO-PET serves also as reference material as that does not corrode in the iodine containing electrolyte. ITO-PET was chosen instead of FTO glass as the former could be cut to the right size to fit the measurement geometry. Using such a stable substrate as a reference is recommended also in literature in order to differentiate between different effects [10].

StS 316 had about 100 mV lower steady state potential compared to ITO-PET (Figure 5). StS 304 had even lower lower steady state potential compared to ITO-PET (about 200 mV difference, Figure 5). A lowering of the steady state potential is caused by corrosion reaction dominating the response. Based on the differences in the corrosion potential, the polarization measurement suggests that StS 304 was clearly corroding, StS 316 was corroding significantly less than StS 304, while ITO-PET was corroding theoretically the least or not at all. The steady state potential measurements are thus in good qualitative correspondence with the literature: StS 304 has systematically suffered from corrosion when it has been applied to the cell without a protective coating [11]. StS 316 without protective coating has reached longer cell lifetimes compared to StS 304, but it has also suffered from corrosion [11]. ITO-PET has been shown to be stable in the electrolyte [4].

Another interesting feature in the measurement was that individual measurements with ITO-PET were completely reversible whereas there was some hysteresis with StS 316 samples, and StS 304 samples were highly irreversible (Figure 5). When corrosion occurs, the oxidized surface of the metal is consumed and the inner non-oxidized metal becomes exposed. The metal oxides on the surface protect the inner parts of the metal from corrosion to a certain extent. When this protective oxide layer is consumed by corrosion, the corrosion reaction gets much faster and that shows as an increase in the corrosion current. This is seen very clearly here with the StS 304 as the back sweep has much higher (corrosion) current value compared to the front sweep (Figure 5a). On the other hand in the case of ITO-PET, there was no hysteresis which suggests that the surface remained intact (Figure 5c).

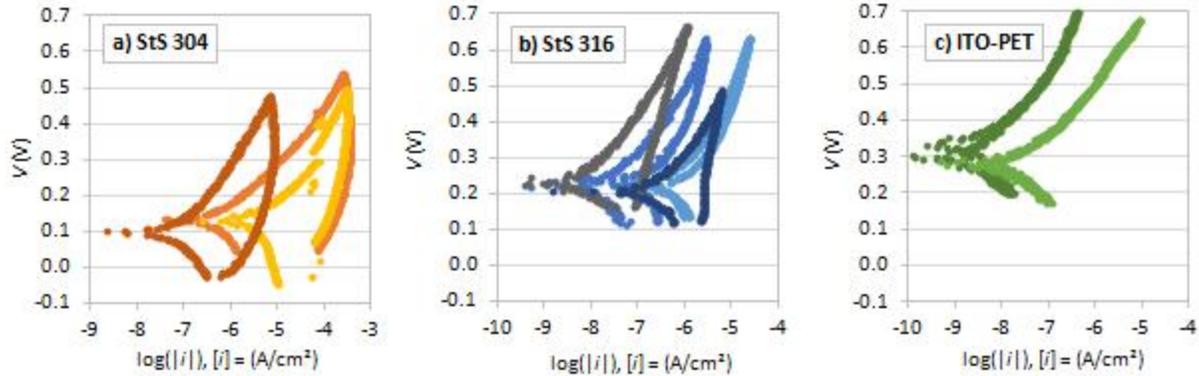
The polarization measurement shows that the steady-state potential is about 0.3 V vs. Pt ref in the case of ITO-PET (Figure 5c) and the extrapolation to give the steady-state current is in the order of 10 nA. The Pt ref used here is not directly in the electrolyte solution, but in KCl which

isolated from the electrolyte with a membrane and thus the potential is not 0 V but 0.3 V. The repeatability of the measured current density varies from sample to sample for all the studied substrates very much, 1-2 orders of magnitude (Figure 5). One of the reasons, in particular for ITO-PET, is that small differences in the surface, such as minor impurities, can have significant difference to the current density as the overall current density is so small. In the case of metals, the variation might lie also in the varying amount of defects that are prone to corrosion, such as the amount of area with lower Cr content, as discussed in Section 3.2. Besides the sample to sample variation, it should be considered that each material has its own charge transfer resistance and thus also steady state current related to the catalytic reaction between the substrate and electrolyte can vary significantly one from material to another. This limits how much can be derived based on the current of the reference measurement.

Since there were clear changes in the steady state potential in the case of StS 304 and StS 316 compared to reference ITO-PET sample, it could have only appeared if the corrosion current was dominating the response in their case. Therefore the measured current at the anodic branch in the case of StS substrates can be with good accuracy approximated to represent the corrosion current. At the steady state potential, the corrosion current at the StS 304 substrate counter electrode would be about  $0.1-10 \mu\text{A}/\text{cm}^2$  (Figure 5a), which is 100-10000 times higher than required for any kind of sufficient stability (cf. Section 3.5). This means that the sample would corrode at that potential between several minutes and a few days.

One of the theoretical benefits of this measurement compared to the previously mentioned ones is that the polarization curve can be extrapolated to more negative voltages for instance to those that correspond to the polarization at the photoelectrode under illumination. However, since there is such a large variation in the measured corrosion current and there is also some variation in the slope of each curve, the error of the extrapolation of the current to OC state at photoelectrode would be several orders of magnitude. Hence such calculations are omitted here.

The positive part of this kind of measurement was the amount of information gotten in a short period of time. The method gives more information compared to the tests used for spontaneous corrosion. One major drawback is that even this method is not sufficient for proving a metal stable enough since in the case of a stable enough metal the catalytic performance can easily be one order of magnitude larger than the corrosion current if and they cannot be decoupled. Hence long term aging measurement would still be needed to prove the sufficient stability in dye solar cells. This method has also the drawback that large volumes of electrolyte are needed as the idea is to have enough of the solution so that it can be regarded to remain constant. To keep the measurement as accurate as possible, it is best to change the electrolyte to a new one between each measurement. Here 150 ml of electrolyte was used for each measurement, which is in fact a relatively small amount for this type of measurement, and in total a couple of liters of electrolyte were needed to make this study. This is a significant issue when investigating novel redox couples that are still synthesized in small quantities.



**Figure 5. Tafel plots showing the polarization measurements of a) StS 304, b) StS 316, and c) ITO-PET. The figures show 2-4 measurements with different samples of the same type of substrate to indicate the repeatability of the measurement.**

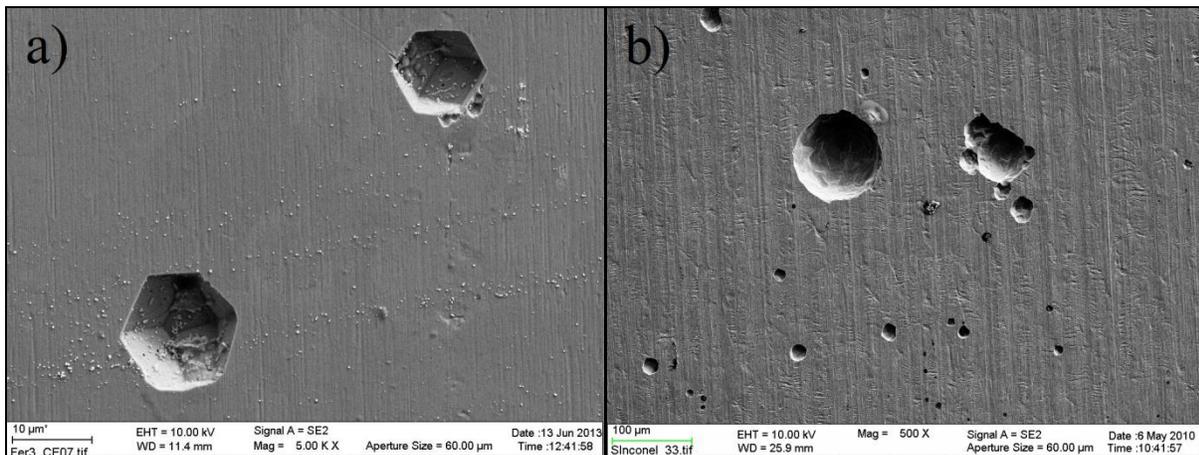
### 3.7 Corrosion in complete cells

The above analysis shows none of the investigated techniques were adequate to prove that a metal would be stable enough in complete DSCs in different operational conditions. The corrosion measurement methods could be used to distinguish metals that are clearly not stable enough to be used DSCs. So the other methods can be used for making the list of metals to be tested in complete solar cells shorter, but eventually the testing of the metals in complete DSCs is still needed to prove the suitability of metals to this application.

Typical signs of corrosion in a complete solar cell are the loss in photocurrent and the loss of electrolyte color. Similar effects can result by other causes besides corrosion such as bleaching of the electrolyte by UV light [26] but also related to other aging reactions [29,30]. Thus a more detailed analysis of the cells is needed to verify the cause for the change of electrolyte color. One way to investigate this is to take SEM images of the metal surface and look for any changes. As stainless steel often corrodes in a way that leaves visible pits on the surface due to localized corrosion, their formation in the aging of the cell verified by investigating the metal before and after aging test is a clear sign of corrosion [11,12]. In some cases also grain boundary corrosion has been seen [9].

The comparison for the metal surface that has not been subjected to the electrolyte (i.e. having “before” comparison) is important as the preparation processes of the metal can leave pits on the surface (Figure 6a) which can be indistinguishable from the pits caused by corrosion (Figure 6b). The pits in Figure 5a are more angular than the corrosion pits in Figure 6b, but this is not a clear differentiating factor between them as corrosion pits can also be quite angular as the corrosion progresses along grain boundaries [12]. The pits in Fig. 6a, e.g., are most likely a result of removal of non-metallic particles or carbides and/or nitrides from the surface during manufacturing of the steel. Commercial grade steels always contain small amounts of non-metallic elements, which cannot be fully removed from the steel. Also, the steels contain small amounts of C and N, which readily form carbides and nitrides. If there are pits initially on the metal surface, consequently the presence of similar pits on the aged metal surface is not an evidence of corrosion. Furthermore in such a case, it is difficult to say that there are no

additional pits of similar size caused by corrosion and further investigation is needed. Another type of corrosion that is also difficult to detect from investigating only the metal surface is the general corrosion i.e. even consumption of metal surface. In such a case there are no detectable changes in morphology of the metal surface. In that type of cases, where the presence of corrosion cannot be seen from the metallic surface, the corrosion has been verified by the presence of apparent corrosion products in the other parts of the cell [9]. There has been apparent corrosion products found e.g. on a glass based photoelectrode due to the corrosion at the counter electrode also all the cases where there were other clear signs of corrosion [9,12]. The other indicators can be affected by other effects than corrosion, but the corrosion residues at the other parts of the cell cannot be explained with anything else. Furthermore, in all the reports where this indicator of corrosion has been studied, it has been present in all the cases where corrosion has been detected [9,12]. Therefore SEM imaging combined with elemental analysis (EDS) is very useful in verification of possible corrosion reactions, but it can also be used to gather evidence of corrosion not occurring, if no corrosion products are found in any of the other parts of the cell [9,12,31].



**Figure 6. a) Example SEM image of a metal surface (Stainless Steel EN 1.4016) with pits that are typical for that metal surface i.e. not caused by corrosion. b) Example SEM image of a Inconel alloy 600 surface corroded by iodine electrolyte (no pits initially).**

Based on the literature, the application of the metals to complete devices and putting them under illumination has been the toughest test to investigate corrosion and directly related to actual use. For instance in the case of iodine electrolyte, only Ti has proven to be stable metal to be used as a counter electrode substrate without additional blocking layers in such testing [12]. The light soaking tests typically are conducted under 1 Sun illumination for 1000 hours and in such test the cells are exposed to the amount of sunlight they would get approximately during one year in outdoors (in Northern Europe). For the effects that are directly related to the amount of light (e.g. degradation by UV), the 1000 hours light soaking test effectively shows the stability for 1 year (about 10 times longer period of time) and it is an accelerated aging test from that perspective. However, since the light does not directly affect corrosion, it is difficult to say how the effect of the light combined with different operational conditions would scale. It may be that

the 1000 hours light soaking test in regards of corrosion reaction is related to only 1000 hours in real outdoor conditions. The prediction for longer periods of time than the actual measured time is missing for corrosion from the literature.

Here we suggest how some prediction could actually be made based on the 1000 hours light soaking test. The idea is to combine analysis of electrolyte color as a part of the analysis; if there was a constant rate of corrosion, there should be a corresponding change in electrolyte color at least in the case of iodine electrolyte. In practice we suggest the combination of the light soaking test of complete cells with the similar color analysis as used in the electrolyte soaking in “cell type” configuration. Since there is typically an excess of charge carriers in the electrolyte, there can actually be quite significant loss without it having a significant effect on the cell performance. Hence looking only at the performance of the cell does not actually give as much information of the loss of charge carriers as compared to the change of cell color [26,32].

In Section 3.4, it was described how electrolyte soaking test could be performed in cell type configuration and investigating the corrosion based on electrolyte color. The same principles could be applied here and the change of electrolyte could be recorded for instance using camera method [26]. It, however, must be taken into account that in the complete cells there are multiple factors that can affect the electrolyte color [30]. To enable the differentiation of the causes for electrolyte bleaching, cells that are not inherently subjected to corrosion (glass cells) should be made and aged simultaneously with the metal cells. The difference in color between the reference and metal cells would indicate the amount of color change related to corrosion. Based on that, the related corrosion rate and the lifetime can be extrapolated. This kind of optical analysis should work well for the iodine electrolyte, but it might be more challenging for the alternative electrolytes. The accuracy of the measurement was given earlier in Section 3.4 and as deduced there, it should easily be possible to detect if the stability was sufficient to be used in dye solar cells for more than 1 year. If the detecting accuracy was 3 %, which should still be achievable, we could predict stable performance for over 5 years. The goodness of the lifetime prediction is mostly affected by the fact that a constant progression of corrosion needs to be assumed; the goodness of that assumption dominantly defines the goodness of the lifetime prediction. As discussed in Section 3.2, typically non-alloyed metals have almost perfectly constant rate of corrosion and for those this kind of analysis this prediction can be highly accurate. For those metals that do not corrode at a constant rate, such as many alloyed metals, the situation is not that clear and in their cases this kind of analysis answers the question that do the metals have *potential* to reach long lifetimes.

## 4. Conclusions

A major finding in this contribution is that the definition of good corrosion resistance in dye solar cells is way beyond what is generally regarded as excellent corrosion resistance; the corrosion penetration rate needs to be 10000-times slower compared to the general “excellent case scenario”. This is because in the case of dye solar cells, unlike in most applications, the performance degradation due to corrosion is mostly related to the consumption of the charge

carriers (i.e. material that corrodes the metal) and not on the consumption of metal. Due to the demanding stability requirement, many of the conventional corrosion tests cannot be used to verify if a metal is stable enough as their accuracy is not sufficient. The conventional corrosion tests are, however, useful in detecting those metals that are definitely not good enough to be used in dye solar cells. Furthermore, since the limit for sufficient corrosion stability is so high, also electrolytes, that are generally regarded not be corrosive, have actually corroded significantly some metals in dye solar cells.

The review of the methods shows that there are clear differences in the capacity of different methods to indicate corrosion. In the case of detecting spontaneous corrosion, electrolyte soaking in cell type geometry and basing the analysis on the color changes was seen as the most accurate method among the different options. It is, however, important to also consider the effect of polarization to evaluate the stability in working conditions. In that regard, a lot of hopes were placed on corrosion polarization measurements and among the conventional methods to analyse corrosion, it did give most information about corrosion in dye solar cells. The benefit of that method is that it is short (only a few hours) and it gives more information compared to the tests used for spontaneous corrosion. However, there were limitations due to repeatability of the measurements and due to other currents than corrosion current affecting the response. Because of the latter reason, even this method could not actually be used to verify that a metal was stable enough.

Application of a metal to complete solar cell and testing that in working conditions was shown as the only way of determining if a metal was stable enough. The conventional way of doing that testing would not allow extrapolation for the future performance which is a major drawback from practical point of view. Here it is proposed that adding also a quantitative color analysis as part of those measurements they could be extended also to give estimates on lifetimes. It was calculated that a 1000 hour test could predict stable cell performance for over 5 years of use.

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