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To cite this article: J Walter *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **706** 012008

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# Electrochemical impedance spectroscopy analysis of iodine/potassium iodide electrolyte influence on spin-coated platinum counter-electrode on FTO glass

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**Abstract.** Very low concentrated precursor solution has been carried out for producing catalytic platinum layers by a spin-coating method. Direct deposition of platinum nanoparticles from low concentrated precursor solution on a conductive substrate results in many nanoparticles remaining in solution. They are not adhesive enough to be able to load them onto another submerged element. The spin-coating method has been applied to use them for catalytic layer preparation. Electrochemical impedance spectroscopy measurements were carried out using a symmetrical setup with the test electrolyte showing, in general, the better properties if more layers are applied. The circuit model for the symmetric setup, containing two identical Pt layers with electrolyte between them, has been proposed. It was found deteriorating layer properties expressed by charge transfer resistance increasing while the platinum layers were influenced by the electrolyte due to a decrease in the amount of platinum on the electrode surfaces. Layers of platinum retain their properties for some hours in contact with electrolyte without measurable decreasing of properties. The spin-coated platinum layer obtained by described method can be used in laboratory tests of Dye Sensitised Solar Cells different components filled with iodide-triiodide electrolyte.

## 1. Introduction

Dye sensitised solar cells (DSSC) may consist of various kinds of counter-electrodes (CE) which are crucial for the cell operation [1-3]. The efficiency of the processes, which require catalysts, depends on the active surface of the catalyst. Platinum is frequently used to improve the charge transfer from the fluorine doped tin oxide glass (FTO) to the electrolyte in DSSC cells and can be also used in various application as a catalyst [4]. A reduction of the costs associated with the use of a platinum, has led to the search for platinum with an extremely high surface area. The application of platinum nanoparticles provides very good catalytic properties and a relatively low cost of material. The counter electrode for a DSSC application is usually prepared by spreading hydrogen hexa-chloroplatinate isopropanol solution on FTO glass substrate [5].

One of the frequently used methods for obtaining platinum nanoparticles is a bottom-up method known as the polyol process [6]. Platinum nanoparticles with a size of a few nanometers, characterised by very good catalytic properties, can be formed during this process. They can be used as a catalyst in



dye sensitised solar cells [7, 8, 9]. The polyol process is based on the chemical reaction between the polyols and precursors, which are the source of nanocrystalline platinum [10, 11]. The most widely used precursors are the platinum chloride  $\text{PtCl}_4$  or potassium hexa-chloroplatinate  $\text{K}_2\text{PtCl}_6$ . The concentration of the nanoparticles in solution, after the process, depends on the amount of precursor used. Using high concentrations of the precursor results in a high material cost. That is suitable for the preparation of pastes for use in a screen-printing technique and economically justified because pastes may consist all formed nanoparticles. This method of obtaining platinum layers can be applied in mass production.

Fabrication of platinum catalytic layers on small scale can be realised by direct deposition of platinum on the substrate, during their formation process, by immersing the substrate in the solution while the polyol process is in progress. This process requires much less of the precursor compare to its concentration required for mentioned screen-printing technique and is very convenient for a laboratory tests. However only a small amount of the formed platinum nanoparticles from low concentration of precursor solution are deposited on the conductive substrate during the process, providing its electrocatalytic properties. Many nanoparticles remain in solution after direct deposition. Remaining nanoparticles are not adhesive enough to be able to load them onto another submerged element. These particles can be used for the preparation of an electrocatalytic layer applying spin-coating method. The proposed method of obtaining catalytic layers based on remaining nanoparticles reported in this study is a very convenient procedure for producing catalytic layers and useful for laboratory tests. Once obtained nanoparticles can be stored in a vessel and used for preparing an electrocatalytic layer when it is needed. The usage of spin-coating of remaining in the solution nanoparticles provides good repeatable catalytic properties for an experimental DSSC cell. Electrochemical impedance spectroscopy (EIS) is frequently used for the evaluation of electrode properties, fuel cell's characterisation or for checking the properties of different capacitive objects [12, 13] as well as for the assessment of dye sensitised solar cells and counter-electrode properties [14, 15]. EIS was used in our work to estimate the electrocatalytic properties of obtained platinum layers. The influence of the platinum layer time in contact with the electrolyte was tested to find long time stability of layer properties.

Mechanisms of the electrocatalytic properties of platinum have been reported in the literature. One of these results showed platinum instability in iodide/triiodide redox couple [15]. However, over the past several years, the iodide-triiodide electrolyte has been the most frequently used as contained the universal redox couple, because of its satisfactory kinetic properties. Other researchers have shown some disadvantages of Pt, like high cost, low abundance and poor corrosion resistance against an iodine based electrolyte. It was reported that the Pt reaction with iodine ions, which forms  $\text{PtCl}_4$  or  $\text{H}_2\text{PtCl}_6$ , causes a degradation of the electrocatalytic activity of platinum [16, 17]. Other research has shown vapour deposited Pt on FTO does not seem to be stable in an electrolyte containing dissolved  $\text{LiI}$  and  $\text{I}_2$ , while solid Pt wire was found to be stable, and did not dissolve, after exposure to the electrolyte [18]. That may be a result of the nano-size of the vapour deposited Pt. Other work showed a drop of current density, for triiodide reduction, of up to 40% caused by the storage of Pt obtained from thermal decomposition of  $\text{H}_2\text{PtCl}_6$  in electrolyte solution [19].

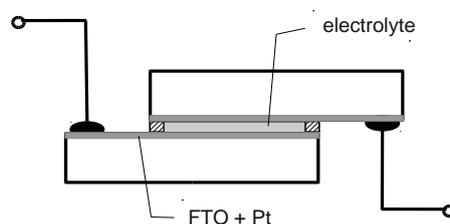
## 2. Material and Methods

### 2.1. Material

Nanoparticles were prepared by a polyol process using 0.001 M solution of platinum chloride  $\text{PtCl}_4$  (Merck), and polyethylene glycol PEG600 (Fluka). The process was carried out for obtaining platinum layer on immersed before process FTO glass at the temperature of 380K for a duration of 60 min. During the heating process platinum nanoparticles were formed in solution and deposited on conductive side of FTO glass. Remaining in solution nanoparticles was further used for layer preparation using spin-coating technique.

## 2.2. Methods

X-ray Powder Diffraction (XRD) measurements of the produced nanoparticles were conducted to check the crystal lattice structure and its parameters. A spin-coating technique, at 3000 rpm for a duration of 20 s, was used, sequentially, to produce one, two and three layers of platinum nanoparticles on conductive side of FTO glass (TEC 15), drying each layer at 390 K before the next loading. Remains of the PEG600 in produced layers were finally removed in the end by heating at a temperature of 720 K for 30 minutes. Distribution of the nanoparticles on the surface was analysed using energy-dispersive spectrometer (EDS) IXRF Systems Model 500 Digital Processing, and the light transmittance of each layer was checked before the main EIS measurements. The layers were used to prepare symmetric cells for EIS two electrode measurements. The cells consisted of two identical Pt layers, formed on the FTO glass, which were facing each other. The distance between FTO-Pt electrodes, each of which were 1 cm<sup>2</sup> in surface area, was about 25 μm, with this gap being filled with electrolyte (figure 1). Similar cells, used by other researchers, have been reported in the literature [20, 21, 22]. The benefit of these cells is that only a small volume of electrolyte is required to conduct measurements. The cell volume was enclosed in Surlyn 1702 heat-sealing foil (Dupont) which separated the electrolyte from any atmospheric influence. The EIS investigations were conducted using a basic electrolyte based on iodine and potassium iodide. The final composition of the test electrolyte contained 0.5 M potassium iodide and 0.05 M of iodine in a solution of polyethylene glycol (PEG 600). Measurements were taken consistently up to after 40 days (961 h) to check the influence of the electrolyte on the electrocatalytic properties of platinum. The cells were then disassembled to measure the transmittance of light through the platinum layers influenced by the electrolyte to check the surface coverage by the platinum nanoparticles.



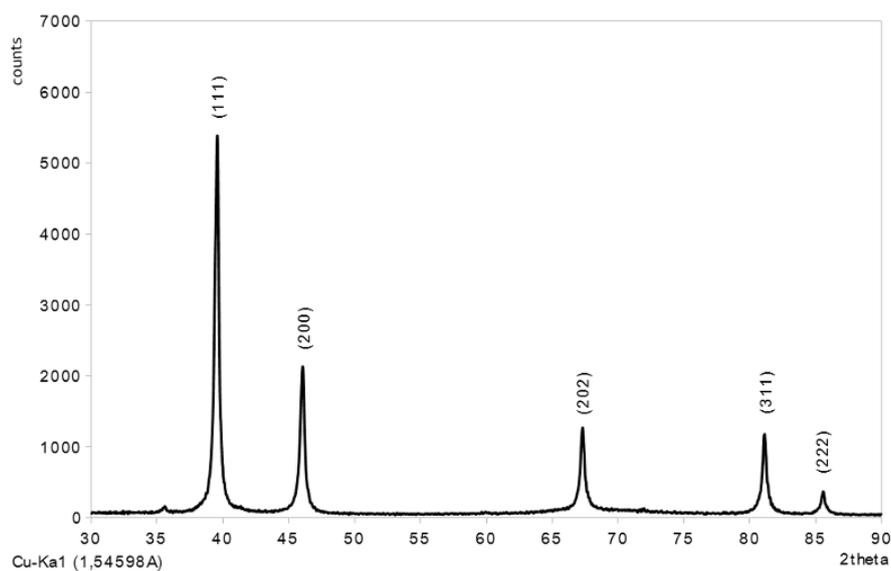
**Figure 1.** Electrochemical cell used for the measurement of impedance spectrum.

The crystal lattice structure of the platinum nanoparticles, produced by the polyol process, was examined using a Bruker diffractometer using ICDD (International Centre for Diffraction Data 2016). The crystal lattice parameter of the platinum was calculated using the Bruker Diffrac software from the half-peak width of the diffraction pattern. The distribution of nanoparticles has been checked on JEOL JSM 820 Scanning Electron Microscope on the FTO glass and analysed by the image analysis method on a surface of approx. 20 μm<sup>2</sup> using ImageJ software. Mapping time, at a magnification 15000 x, was set to 1.5 h for all samples to verify platinum loading.

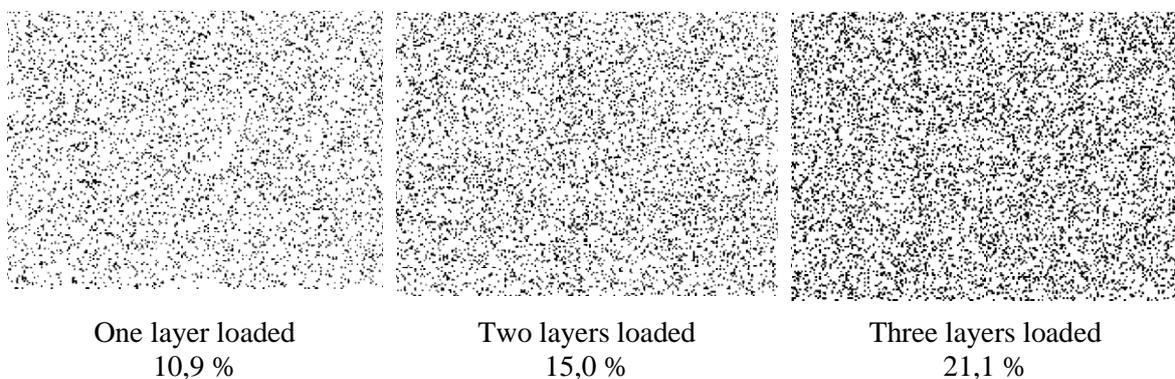
EIS examinations were carried out using Zahner IM6e device to characterise the differences between cells (I, II or III layers of Pt) and check the catalytic properties of the platinum layers and stability of them over time. Measurements were conducted in the frequency range of 1 Hz to 1 MHz, applying a 5 mV AC voltage amplitude. The electrical circuit model for obtained fitting the curves has been proposed using the SIM module Zahner IM6e electrochemical workstation. The same, or similar, models have been proposed in other research [20, 21, 22].

### 3. Results and discussion

The results of X-ray examination are shown in figure 2. Diffraction tests showed platinum-specific peaks. The exact value of crystal lattice parameter was equal to 0.3923 nm, which was consistent with the database. The result of this calculation showed that the crystalline size was about 6 nm. Analysis of the distribution of platinum on the FTO glass surface was carried out using EDS to compare the loading of the platinum after the spin-coating cycles. An almost homogeneous coverage of the FTO substrate was found with the tested layers having different amounts of nanoparticles on each sample, corresponding to the number of applied spin-coating cycles (I, II or III cycles). The mapping results are shown in figure 3. The result of EIS investigations of the symmetrical cell setup (figure 1) of the FTO plate, with one layer of platinum using the spin-coating technique is shown in figure 4. Cells built using two and three layers of platinum are shown, respectively, in figure 5 and figure 6.

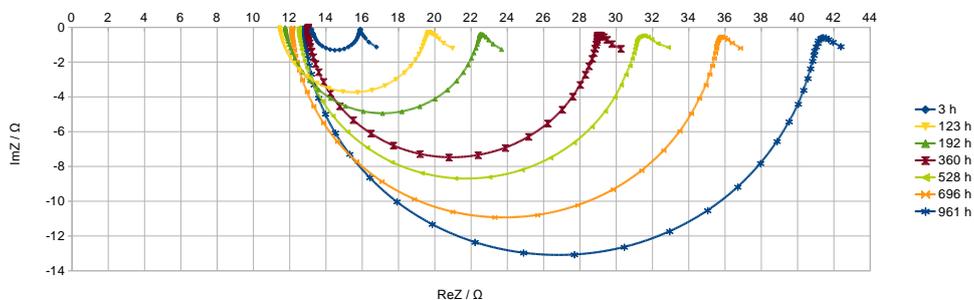


**Figure 2.** X-ray pattern of platinum nanoparticles.

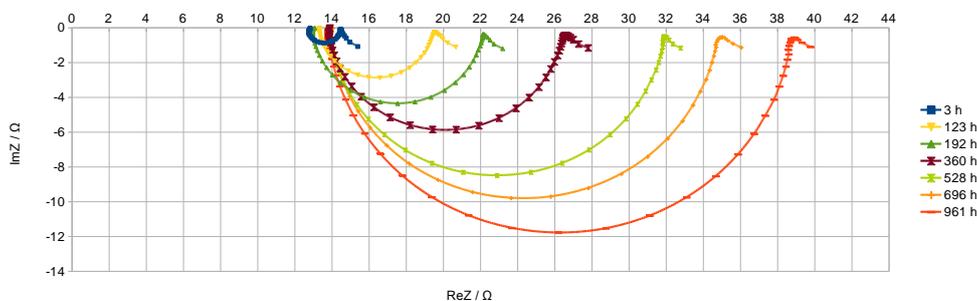


**Figure 3.** Coverage of the surface by nanoparticles of platinum, expressed as a percentage.

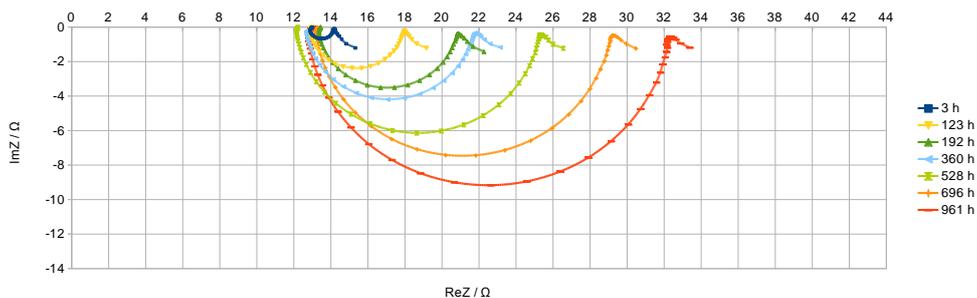
The curves shown in figure 4, 5 and figure 6 showed the charge transfer resistance describes by arcs on graphs and Warburg impedance visible at highest values of  $ReZ$  as a straight line at the angle  $45^\circ$  to the axis. It is noticed on graphs that charge transfer resistance value increases over time – the arcs increases.



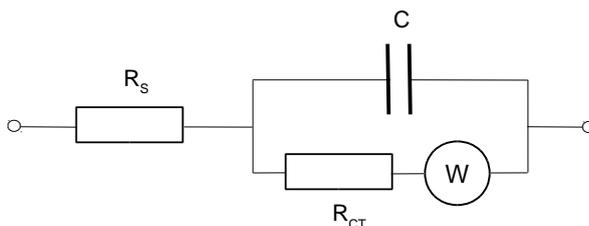
**Figure 4.** Nyquist plot of cell consist one Pt layer vs. time of electrolyte influence.



**Figure 5.** Nyquist plot of cell consist two Pt layer vs. time of electrolyte influence.



**Figure 6.** Nyquist plot of cell consist three Pt layer vs. time of electrolyte influence.



**Figure 7.** Equivalent circuit for the impedance spectrum in the cell.

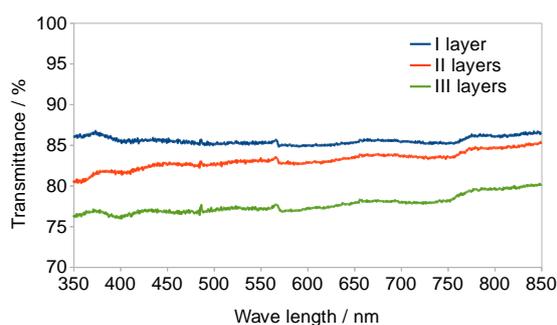
A circuit diagram, and its components, is shown in figure 6. The schema consists of a series resistance ( $R_s$ ) which corresponds, mainly, to the resistance of the electrolyte and the resistance of the connectors. The second element, labelled  $R_{CT}$ , is a charge transfer resistance which is convenient for describing the platinum layer properties for DSSC applications. Capacity ( $C$  on this schema) characterises the phenomenon that occurs near the electrode surface and the Warburg diffusion element ( $W$ ) models the diffusion processes that were observed at the lowest frequency.

The values of elements, calculated by dedicated SIM software, versus time are shown in Table 1.

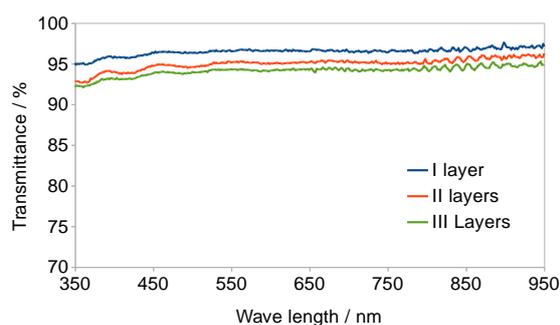
**Table 1.** Values of schema elements over time calculated for I, II and III layer of platinum.

element	1 – 4 h*			124 h			961 h		
	I	II	III	I	II	III	I	II	III
$R_s$ ( $\Omega$ )	12.8	12.3	12.1	11.6	13.4	12.9	12.9	13.9	12.9
$R_{CT}$ ( $\Omega$ )	3.0	1.6	1.2	7.8	6.0	4.9	27.6	24.4	19.1
$W$ (DW)	4.2	3.8	4.3	4.5	4.1	4.3	5.0	4.6	4.3
$C$ ( $\mu$ F)	4.9	4.9	9.0	5.6	7.2	8.3	3.9	4.7	5.9

\* mean values calculated for first 4 h



**Figure 8.** Transmittance of the FTO/Pt counter electrode with different loading of Pt before layers exposure in electrolyte.



**Figure 9.** Transmittance of the FTO/Pt counter electrode with different loading of Pt – influence of electrolyte.

It was found that the series resistance,  $R_s$ , did not change significantly during the time of the electrolyte contact with the platinum layers in all the tested cells (Table 1). The  $R_s$  value oscillated in a range from 12 to 14  $\Omega$ , mainly due to the fluctuation of an electrical connections resistance. The mean value of the series resistance, for all the measurements, equal to 12.8  $\Omega$  is a result of the conductivity of the applied electrolyte and its ion concentration. Significant changes in  $R_{CT}$  values were observed in measurements carried out on each cell. Table 1 shows differences between cells built from I, II or III layers.  $R_{CT}$  strongly depends on the loading of platinum on the FTO substrate and the time of electrolyte influence on platinum layer. During the first hours of the iodine/potassium iodide electrolyte influence on the Pt layers the value of charge transfer resistance was stable. Its value was lowest for III layers and highest for I layer (Table 1). The best electrocatalytic properties were obtained for a higher loading of platinum. The mean values of  $R_{CT}$ , calculated for the first four hours, were 3.0  $\Omega$ , 1.6  $\Omega$  and 1.2  $\Omega$ , respectively, for I, II and III layers. Further measurements were taken after much longer periods of time to check the stability of the layer properties. An increase of  $R_{CT}$  with an increase of time was found. Its value, after 124 h, seems to be too high to apply these layers in solar cells because of possible drop of current result in lower efficiency of solar cell. With an increase in time, the  $R_{CT}$  showed much higher values for all tested layers. The cell consisting of III layers was characterised by better properties than the I and II layer cells, but values were not acceptable: I layer – 27.6  $\Omega$ , II layers – 24.4  $\Omega$ , and III layers – 19.1  $\Omega$ , after 961 hours. Compared to the  $R_{CT}$  changes, the

Warburg impedance did not change significantly. This is also shown in figure 4, figure 5 and figure 6. The double layer capacity (C) depends on the platinum loading. The highest capacity was found for a higher amount of Pt with its decreasing over time. The same dependence can be seen for a smaller platinum loading (I layer). The most important changes observed in this study are the changes in the  $R_{CT}$  value with increasing time. Using UV/Vis spectroscopy applied for this purpose by other researchers [23] the differences in loading of platinum, before preparing the symmetrical setup, was checked by measuring the transmittance of light through the FTO glass covered by I, II and III layers (figure 8). The highest transmittance (about 85 %) was found for I layer of platinum which is a result of the lowest loading of Pt. The electrocatalytic properties of Pt loaded on an FTO substrate deteriorated with increasing exposure time to iodine/potassium iodide electrolyte. A larger loading of Pt did not resolve the problem. It was found the same phenomenon in all three type of layers (I, II and III) with different amount of Pt. The increases of  $R_{CT}$  are a result of the decreasing of nanoparticles number on FTO surface, which in the effect of electrolyte contact influence. That has been confirmed by transmittance measurements. A much higher transmittance of the Pt layers after 961 h exposure in the electrolyte, compared to the same layer before exposure, was found (figure 9). That is a result of decreasing of platinum amount of FTO surface which cause the increases of values of the charge transfer resistance  $R_{CT}$ .

#### 4. Conclusions

Platinum counter electrodes, prepared by a spin-coating technique from a low concentrated solution containing nanoparticles of Pt, are characterised by good electrochemical properties, depending on the platinum loading and the time of iodine/potassium iodide electrolyte influence. Reported in this work results showed that described method can be used for preparing counter electrode only for laboratory tests which could be useful for DSSC cells examination. Platinum electrocatalytic layers obtained by this method provide good stability over time during first 4 hours after preparing which is enough for taking measurements. The advantages of this method is possibility of preparing very low concentrated solution of the platinum nanoparticles and use them for layer preparation when it will be needed. The best electrocatalytic activity, for triiodide reduction, was found for a higher platinum loading (III layers) by spin-coating. Charge transfer resistance  $R_{CT}$  was satisfactorily low. The influence of the electrolyte on the Pt counter-electrode, results in a significant increase in the  $R_{CT}$  value with increasing time. This is a result of the smaller amount of platinum nanoparticles adhering to the FTO, which was illustrated by the transmittance measurements. The same results were found for all the tested loadings. To summarise, counter electrodes can be prepared using the low concentrated Pt precursors in polyol process and the obtained Pt is suitable for testing dye sensitised solar cells because it has good electrocatalytic properties, for a sufficiently long time, to enable exact measurements to be taken.

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