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Properties of screen-printed modified graphite layers

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Abstract

During last years protection of the environment is one of the important problems that should be solved by modern technology. The important problems are toxic gases emitted by conventional power plants. One of the methods that contribute to decreasing air pollution is manufacturing of cheap solar energy devices that could be applied in households. Among different type of fabrication technology of solar cells, DSSC technology looks like one of the interesting because it is relatively simple and low cost technology. Nowadays a lot of researcher groups making investigations to improve its setup, to get the cost reduction. The methods to achieve this goal were proposed in ISE (Germany) as a concept of monolithic dye sensitised solar cell. One of the ideas of this solar cells setup is replacing expensive TCO electrode by much cheaper graphite electrode. Replacing TCO glass by graphite layer has to be done only in case of comparable properties of those both electrodes. There are some tested ideas of manufacturing that electrode and some of them are successfully applied. Presented work has been focused on preparation graphite conductive electrode for DSSC technology application, fabricated by screen–printing technique. Investigations concern new graphite past composition suitable for graphite layer preparation. It was been found that applying additive of titanium organic compound (Tyzor GBA) to the past composition result in good properties, characterised by low resistance and good adhesion between graphite particles in the printed layer. Some tested layers prepared from proposed paste compositions characterised by better conductivity then applied in conventional DSSC cells counter electrode. The optimal addition of the modifier has not fixed yet. Among tested pastes the most promising results has been achieved for paste contained the biggest amount of Tyzor GBA.

Keywords: environment protection, solar cells, conductive layers, screen printing, graphite

1. Introduction

The research on Dye Sensitised Solar Cells has been started in 1991 by discovering that sensitising titanium dioxide photoelectrode covered with organometallic dye can useful for fabrication of photoelectrochemical cells. Power conversion efficiencies about 5 to 12 % can be achieved in dependence of cell size and its setup. Most of the research work on DSSC for the last several years has been focused on standard sandwich type cells. Main factors that were limiting device dissemination are costs and performance of them. New material concepts and cell setup are still needed. Invented last time by German researchers new monolithic setup of DSSC is a one of the interesting low cost technologies of fabrication photovoltaic devices. Proposed solar cell setup is based on similar component known from sandwich type of devices. The main difference is applying graphite counter electrode that is low cost conductive layer screen-printed on non expensive glass. Typical setup of that cell has been shown on Fig. 1. The monolithic cell consists two glass plates characterised different conductive layer applied. One of them is so called TCO glass that is covered with transparent SnO_2 fluorine dopped conductive layer. The second is typical glass on which conductive layer has been printed using graphite paste. Between these two electrodes are situated semiconductor and separation and catalytic layers. The cell is filled with specially designed for this purpose electrolyte. Conductive layer which is a topic of this work should characterised by relatively low resistance and very good adhesion between graphite particles as well as graphite to the glass plate. We proposed in this work titanium contain organic compound as a modifier of graphite paste composition.

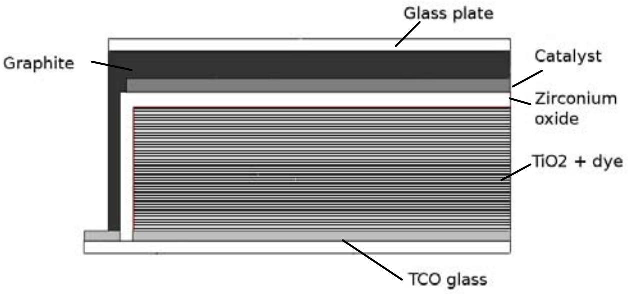

Fig. 1. The monolithic setup of DSSC cell

The good adhesion of graphite layer is necessary because of moving particle in cell volume that cannot be accepted due to harmful influence on photovoltaic cell efficiency.

2. Experimental

2.1. Paste composition

The graphite pastes were fabricated by mixing graphite powder (Timrex SFG 44) and organic substance contained titanium called Tyzor® GBA with water free binder. The binder was prepared by dissolving ethyl cellulose (30 – 60 mPa·s, Fluka) in terpineol. Pastes were homogenising in high speed spindle mixer up to obtaining homogenous consistency. That takes place after 2 hours of mixing with 8500 rpm. The binder is well known standard solution of organic substances applied in DSSC technology. Its composition based on ethyl cellulose and terpineol has been modified by different amount of titanium compound that should result in improvement of adhesion between graphite particles as well as adhesion of graphite to the substrate in assumption. Composition of tested pastes was shown in Table 1.

The liquid titanium contain organic substance (Tyzor GBA) contained in higher concentration in binders result in decreasing viscosity. That caused necessity of controlling loading of ethyl cellulose to keep viscosity it on the same level. The viscosity of the basic solution with modifier was maintained about 3000 mPa·s.

Table 1.
The graphite paste composition

Paste	Content (wt %)		
	Graphite	Tyzor GBA	Binder
P1	50	0	50
P2	50	2	48
P3	50	4	46
P4	50	6	44
P5	50	8	42
P6	50	10	40

2.2. Layers preparation

Fabricated pastes characterized by good castability were found as usable for screen printing technique. The hand operated screen printer was used for graphite layer fabrication .Because of graphite particle size, D90 equal to 44 – 53 µm (technical data sheet) and minimal crystalline size, about 200 nm, polyester screen 105 mesh/inch with hole size of 75 µm was used. Layers were printed on glass plates which are non conductive. Plates were carefully cleaned before printing using detergent and then ethanol. After one stepped screen printing process layers were heated in oxidising atmosphere at the temperature range of 375°C to 450 °C by 30 minutes. In assumption that treatment should fired organic binder what is necessary to fabricate solid conductive layer.

2.3. Characterisation of graphite layers

The applied screens, as well as the ratio of graphite to binder in the paste, determine the layer thickness. Thickness measurements showed that fired graphite layer are 0.07 mm thick. The most important parameter of the graphite layer is the resistance of it. That should be comparable to TCO resistance. Sheet resistance has been checked and additional precise measurements of resistance have been done by using impedance spectroscopy method. Examinations were carried out at frequency range between 10 Hz and 100 kHz in order to check additionally contingent of capacity or inductance, those can occur due to connection between graphite particles.

Adhesion between graphite particles were tested by modified for this purpose pull off method adapted to specific properties of graphite layer. There were applied simple test based on adhesion forces of Scotch Crystal 600 tape to graphite layers. The sheet of tape area of 1 square centimetre was glued with the force of 10 N to the layer and the next removed with adhered to it graphite particles. Lossless of layers weight has been chosen as a criterion of adhesion between particles.

3. Results and discussion

The representative result of impedance measurement measured obtained from on 1 cm^2 surface of graphite layer was shown in Fig. 2. It was found that value of impedance in tested range of frequency stay in the same level. Any significant changes in impedance spectra caused by capacity or inductance has no observed in all checked layers. That shows typical resistance nature of fabricated layers.

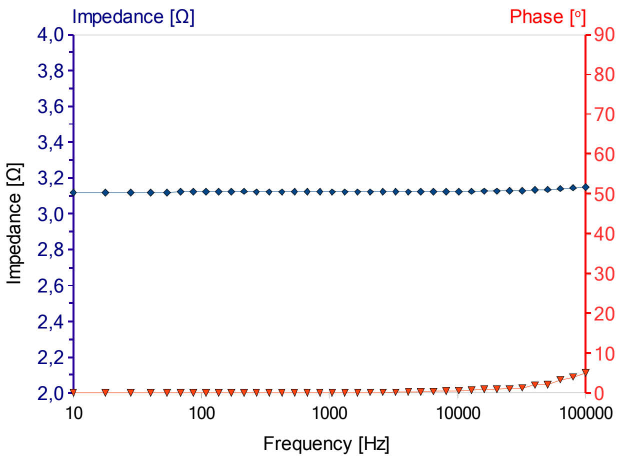

Fig. 2. Impedance spectra of graphite layer fabricated using paste P6 and fired at temperature 375 °C by 30 minutes

Fig. 3 compares conductive characteristics of different layers heated in temperature range of 375 to 450 °C. Sheet resistance of layers strongly depends on temperature of heat treatment. We found decreasing of resistance during increasing of firing temperature for all layers contained different amount of Tyzor GBA. Similar curve characteristic can be observed for two lowest temperatures of treatment, 375 and 400 °C. Those layers resistance is lower then 5 Ω. Compare this value to resistance of TCO glass equal to 6.7 Ω measured using the same method we found promising result. It was shown on graph that the lowest resistance was obtained for layer fabricated from past P6 and treated in the lowest applied temperature. Applying higher then 400 °C temperature caused significant changes in layers properties. Resistance gets much higher values, particularly in layers fabricated form pastes with smaller amount of titanium compound. The worst result has been obtained for Tyzor GBA free paste. Layers obtained from paste without that additive characterised by very low resistance to oxidation. Oxidation of graphite starts in ambient conditions at the temperature about 400 °C, what result in higher resistance.

The positive effect of addition tested compound on oxidation in 450 °C as well as on the resistance in lower temperatures was shown in Fig. 3. Layers manufactured from paste P1 that has no additive of Tyzor GBA strongly oxidise in temperatures over 400 °C but in lower tested temperatures resistance of them has been found on the similar level compare to layers with Tyzor GBA included.

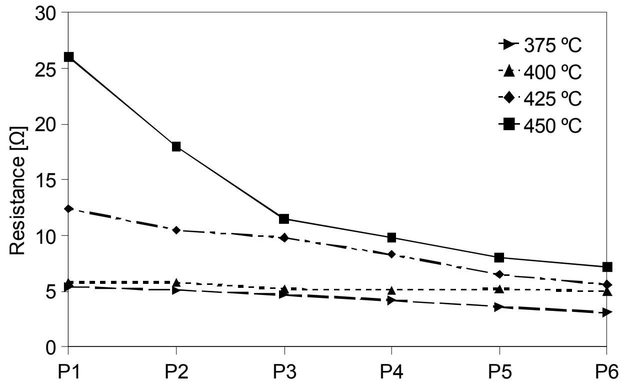

Fig. 3. Resistance of graphite layers vs. paste composition after different temperatures of heat treatment

The addition of Tyzor GBA improved graphite oxidation resistance.

Beside the graphite layer conductivity, very important property of graphite layer is adhesion between particles as well to the glass substrate – Fig. 4. First simple examination shows that layers prepared form pastes that has no any addition of titanium organic compound are characterised by a very bad coherence between particles and can be removed from the substrate surface very easy (P1). Loss of weight tested on surface of 1 cm^2 is about 5,5 mg and a bit higher in 450 °C. These values reached the almost maximum that is possible in applied method.

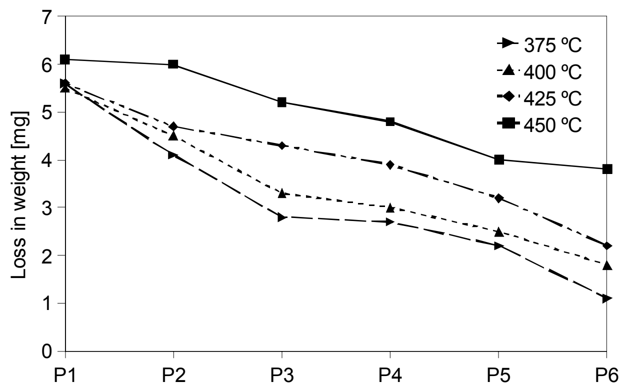

Fig. 4. Adhesive test results: loss in weight vs. paste composition

We noticed that losses of weight of graphite about 5.5 mg shows that particles are not connected to each other. Layer prepared from that past likewise showed not bad result of measured resistance (about 5 Ω at 400 °C) but it cannot be preserved to the next operation because of very low adhesion. Past prepared only from binder and graphite cannot be applied in practice.

Other layers fabricated form pastes with higher addition of Tyzor GBA (P4, P5 and P6) characterised in much better adhesion. The best result of measurement of losses of weight was found for layer prepared form paste P6.

This first examination proved that applying temperature of removing organic binder about 370 to 400 °C and about 10 % addition of Tyzor GBA makes possible to use fabricated that way layers as a conductive layer.

4. Conclusions

Usable graphite layer can be manufactured by screen-printing method. Necessary printable pastes based on standard binder should contain as high as possible content of graphite and have suitable consistence for screen-printing. It was shown that one of the most important parameters in layers fabrication process is temperature of removing the binder from printed layer. In case of graphite SFG 44 treatment in temperatures over 400 °C leads to worst conductivity caused by layer oxidation. The bigger amounts of Tyzor GBA significantly changed adhesion between graphite particles and improve the conductivity even when the heating temperature is too high.

Addition of 6 to 10 % wt. of tested titanium contain organic compound has no big influence on conductivity but we noticed small improvement with higher content of Tyzor GBA.

The main advantage of including tested modifier additive to past composition is improvement of adhesion by about 5 times in the lowest temperature. That looks to be important for solar cell manufacturing technology.

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