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A new method to make dye-sensitized nanocrystalline solar cells at room temperature

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Abstract

This paper describes a new method for manufacturing a nanostructured porous layer of a semiconductor material at room temperature. The porous layer is pressed on a conducting glass or plastic substrate for use in a dye-sensitized nanocrystalline solar cell. The method compresses the particle layer to form a mechanically stable, electrically conducting, porous nanostructured film. Overall, solar to electric conversion efficiencies of up to 5.2% at 0.1 sun using plastic substrates have been obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nanostructured; Solar cell; Electrode; Dye; Photoelectrochemical

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1. Introduction

Dye-sensitized nanocrystalline solar cells (DNSCs) have been intensively studied during the last decade [1–3]. Certified solar power efficiencies of 10.4% [4] and stability data with lifetime expectancies of at least 10 years for outdoor use [5] have been achieved in the laboratory.

High enough efficiency and low production costs are important characteristics to make DNSC modules competitive to other alternatives on the market. However, the efficiency of DNSC tends to stay at a lower level than for, e.g. crystalline silicon cells as well as for the next generation of solid-state thin film technology like CIGS cells.

The competitor to the DNSC cells for indoor applications, not requiring high efficiencies, is the amorphous silicon cell already being produced at low prices in large-scale facilities. The conclusion, therefore, is that much attention has to be given also to the cost reduction potential in possible production technologies for DNSC cells if it shall be able to become commercial in the future.

Several research groups, institutes and companies currently work on developing DNSC products. The process technology used today is based on screen-printing, which is a batch process consisting of 10–15 different steps. A colloidal solution of TiO_2 particles is printed on a conducting glass substrate. The film is sintered at about 450°C which is needed to remove the organic binder and solvent, and to obtain an electrically connected network. The screen-printing batch-based technology has severe limitations for substantial reduction of production costs. In the following, we present our development work with respect to a new way to produce the TiO_2 porous film. This opens up the possibility for a continuous production process for DNSC cells and modules. A continuous production process has generally a high potential for low-cost production.

1.1. The search for a new direction of development of DNSC within Ångström Solar Center

The Ångström Solar Center (ÅSC) is an R&D program for solar energy technologies. It includes thin film solar cells (CIGS), DNSC solar cells and electrochromic “smart windows”. ÅSC started its activities in the fall of 1996. The overall objective of the program is to develop these technologies to a stage where the results can be handed over for a further industrial development.

An analysis of the competitive position of the DNSC cells in the fall of 1996 came to the result that crystalline silicon technologies would dominate the coming decade. Next generation of solar cell technologies will probably be based on thin film technology due to its potential for lower production costs at large-scale manufacturing. The most promising thin film technology at that stage was the CIGS concept, a situation probably unchanged today, 5 years later.

The DNSC group in the ÅSC program therefore early identified the CIGS group of the program as their main competitor. The road to the future for the DNSC group therefore was to enhance properties of a future DNSC cell, which could open up market segments not so easily satisfied

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by CIGS on glass. The long-term goal for DNSC efficiencies was above 10%, lifetime expectancies had to become similar to the CIGS cells and the potential cost reduction in production technology had to become much larger than that for CIGS.

The ÅSC DNSC group therefore also concluded that a shortcut to reach the market would be to focus initially on indoor applications where parameters like efficiency and durability may not be as harsh as for outdoor applications.

For indoor applications, the amorphous silicon cells are conventionally used. In an European union project [6], DNSC modules were prepared by the screen-printing method and tested under typical indoor light conditions. The DNSC cells reached equal or slightly better performance compared to commercial amorphous silicon modules. Our conclusion was that for indoor applications, there is already a reliable cheap technology in the amorphous silicon cells as long as only low efficiencies were needed. Therefore, the DNSC cell had a competitor in place, which were hard to compete with. The conclusion was that the opening up for a DNSC future lied in a combination of an extremely cheap production technique with substantially better cell efficiencies than amorphous silicon and much improved reproducibility in the preparation.

In the fall of 1996 we had two starting points: (i) a good understanding in the group of paper industry technology in which a continuous production technique has been developed and fine tuned during the last 100 years, and (ii) some preliminary preparation experiments of TiO_2 films back in 1993–1994 revealing the possibility to press TiO_2 powder into porous films on conducting glass substrates.

A prerequisite for a continuous web-based process is to use a flexible substrate. The most straightforward material is some type of polymers which can be rolled up. Looking for cheap polymers as the substrate for the cells or modules, high temperatures in the manufacturing process cannot be accepted. The pressing of oxide layers for production of porous thin films was therefore again taken up into a more serious and systematic effort during 1997/1998. The objective was to prepare and produce a nanostructured oxide film at room temperature [7,8].

2. Experimental

In this paper, we discuss results obtained using both glass and plastic substrates. The preparation of the porous layers for the working and the counter electrodes needs to be modified depending on the type of substrate used. The preparative descriptions of the different layers are divided accordingly.

2.1. Working electrode materials

2.1.1. Glass substrates

Degussa P25 TiO_2 powder was added to an amount of 20 wt.% to ethanol. The suspension was applied onto a conducting glass by doctor blading using scotch tape as frame and spacer. The conducting glass substrate was a Tec 8 supplied by Hartford glass and consisted of a soda lime glass sheet with a conducting layer of fluorine-doped tin oxide of 8 Ω/square resistivity.

2.1.2. Plastic substrates

The same TiO_2 solution was prepared, and the same deposition method used, as described for the glass substrates. The conducting plastic substrate was "ITO-60", an ITO-coated PET-based substrate supplied by IST (sheet resistance: 60 Ω/square).

2.2. Counter electrode materials

2.2.1. Glass substrates

The counter electrode consisted of a thermally platinized conducting glass (5 mM H_2PtCl_6 in dry isopropanol, heated at 380°C on a conducting glass substrate for 10 min).

2.2.2. Plastic substrates

Two different counter electrodes were studied: porous carbon and porous-platinized SnO_2. For the carbon counter electrode, 0.8 g graphite powder (99.5%, <325 mesh, supplied by Alfa) and 0.2 g carbon black (Printex L, supplied by Degussa) was ground in a mortar together with 1 g ethanol. Next, 0.36 g P25 and 5 g ethanol were added. The solution was then deposited onto the conducting plastic substrate. For the other alternative, Sb-doped SnO_2 powder (Zelec ECP-3010-XC, supplied by Du Pont) was platinized by mixing 500 μl, 5 mM H_2PtCl_6 in isopropanol with 0.5 g SnO_2 and heating the mixture to 375°C for 10 min. The platinized powder was then crushed and stirred together with 1.5 g ethanol for 12 h. The resulting suspension was then deposited on a conducting plastic substrate.

2.3. Compression of the porous layers

2.3.1. Glass substrates

After evaporation of ethanol from the deposited suspension, the substrate with the attached powder film was put between two planar steel press plates. Pressure was applied by using a hydraulic press. The applied pressure was varied to study the morphological and photoelectrochemical properties as a function of pressure. A typical pressure used for preparation of efficient solar cells is 1000 kg/cm^2.

2.3.2. Plastic substrates

After evaporation of the ethanol, the powder films of TiO_2, SnO_2 and carbon were compressed either statically or continuously. By a static compression, we mean the same procedure as described for glass substrates. For the continuous compression, the nanostructured TiO_2 film was deposited on a flexible conducting plastic substrate using a roll (supplied by Oy Gradek AB in Finland). The compression was performed by allowing the substrate with the deposited powder film to pass the roller nip with a speed of about 1 m/s and with a roller line pressure of 400 kN/m.

2.4. Dye sensitization and electrolyte preparation

The compressed TiO_2 electrodes were dye sensitized by submerging the substrate with the deposited film for 2 h in a dye bath consisting of 0.5 mM *cis*-bis(isothiocyanato)bis (2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)bis-tetrabutylammonium, i.e. N719 dye supplied by Solaronix. The electrolyte consisted of 0.5 M LiI (99.99%, $H_2O < 100$ ppm, Aldrich), and 0.05 M I_2 (99.999%, $H_2O < 100$ ppm, Aldrich) and 0.5 M *t*-butylpyridine (99%, Aldrich) in methoxypropionitrile (99%, Fluka). An alternative electrolyte was used for measurements of plastic solar cells at low intensities simulating indoor light conditions (230 lx, using fluorescent lamps). This alternative electrolyte consisted of 0.5 M LiI, 0.01 M I_2 and 0.5 M *t*-butylpyridine in methoxypropionitrile.

2.5. Photoelectrochemical characterization

The photoelectrochemical properties were investigated by measuring the *I–V* characteristics in a sandwich electrode configuration. The *I–V* curves were monitored and recorded using a computerized Keithley 2400 source meter. To simulate sunlight, a sulphur lamp (Lightdrive 1000 from Fusion Lightning) was used.

3. Results and discussion

3.1. Glass substrates

Preparation of TiO_2 films on glass substrates were made in order to characterize the morphological properties of the compressed films as well as having the possibility to study the effect of a thermal post-treatment to obtain a film resembling the TiO_2 electrodes prepared by the conventional sintering procedure.

Fig. 1 shows a SEM picture of a compressed, nanostructured TiO_2 film. Visually, this picture reproduces the structure obtained by preparing a nanostructured TiO_2 film according to the sintering process. From a morphological point of view, the following characteristic properties were achieved.

Porosity. The powder films were compressed at different pressures. The results from these experiments are shown in Fig. 2. At each pressure, an average porosity of three measurements is calculated. The porosity at 200 kg/cm^2 pressure was 69%, which decreased to about 50% at a pressure of 2000 kg/m^2.

Surface area. BET measurements were performed on P25 powder and on compressed TiO_2 films. Both samples were sintered at 450°C in air for 30 min. The applied pressure was 1000 kg/cm^2. The BET surface area of the compressed film and the powder were 63.9 and 60.6 m^2/g, respectively. This means that the internal surface area increases after compression of the film. This is probably due to cracking of large aggregates of TiO_2 particles. The BET pore size distribution in the compressed film ranged from 5 to 60 nm with a maximum at 23 nm and the average pore diameter was 23 nm. Thus, the pores in the compressed film have approximately the same diameter as the particle size. The average pore diameter of the unpressed powder was 27 nm; however, the pore size distribution was much broader, ranging from 5 to 200 nm having a small and broad maximum at 30–40 nm. The BET porosity value of the compressed film and the powder was 52%, which is in good agreement with the porosity value of 54% obtained by the gravimetric porosity determination at the same applied pressure (1000 kg/cm^2; see Fig. 2).

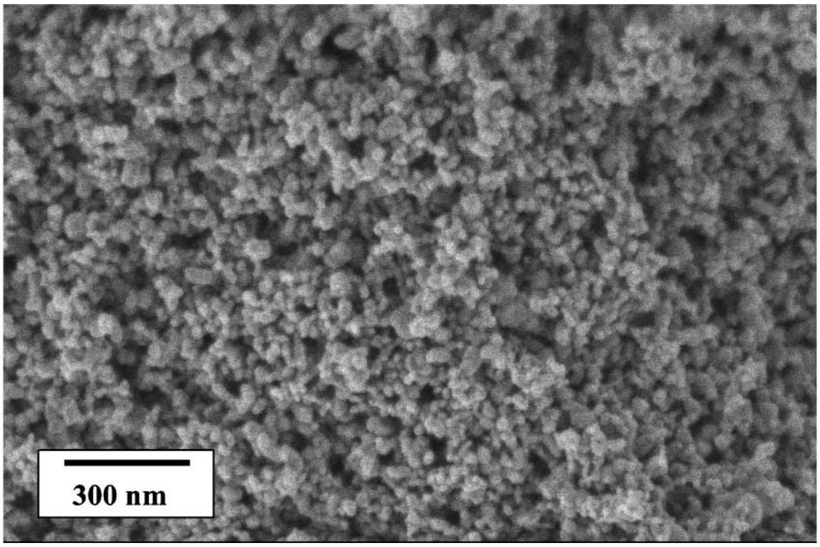

Fig. 1. SEM picture of a compressed TiO_2 powder film.

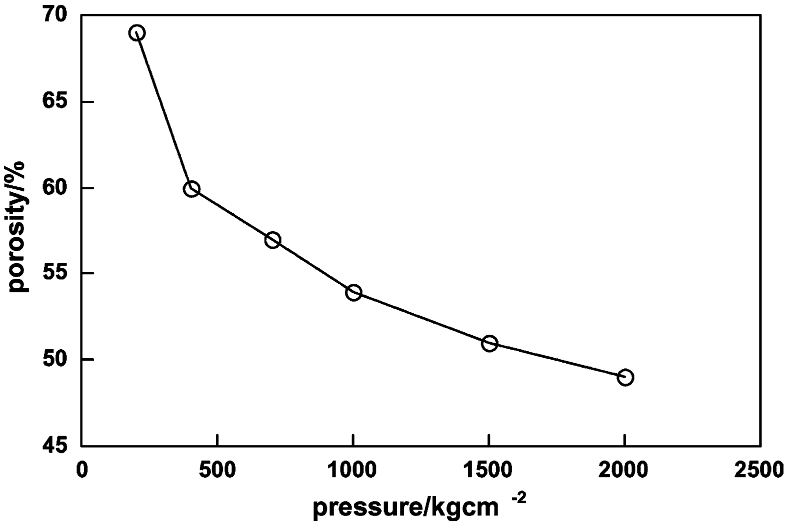

Fig. 2. The porosity of compressed TiO_2 powder films is shown as a function of the applied pressure.

A comparison between compressed films with an additional heat treatment (sintering) and with compressed films not further treated (non-sintered) are given in Tables 1 and 2. The tables show the averaged data extracted from *I–V* curve measurements on compressed dye-sensitized nanostructured 8 μm thick electrodes. The manufacturing parameters for all electrodes were kept constant with the only exception that electrodes in Table 1 were not sintered before dye sensitization, and electrodes in Table 2 were sintered at 450°C for 30 min before dye sensitization.

A comparison between the values in Tables 1 and 2 shows that the *I–V* characteristics of the sintered and the pressed, nanostructured TiO_2 electrodes are similar. The main effect at higher light intensities is a decrease of the fill factor. The short-circuit current, I_{sc}, is almost linear with respect to light intensity. Thus, the efficiency drop at higher light intensities can be attributed mainly to series resistance losses in the conducting substrate.

3.2. Plastic substrates

The *I–V* curve for an all-plastic sandwich cell is shown in Fig. 3. The counter electrode consisted of platinized SnO_2 powder pressed on a conducting plastic substrate. The electrode was produced without using heat treatment. The overall cell efficiency was 4.9%. Because of the series resistance losses in the conducting plastic layer (sheet resistance: 60 Ω/square), it was very difficult to reach high conversion efficiencies with pressed SnO_2 electrodes at higher light intensities. Nevertheless, at 1 sun intensity we reached values for the fill factor, open-circuit voltage and short-circuit current of 0.41, 0.76 V and 7.3 mA/cm^2 (*I–V* data not

Table 1
Compressed non-sintered electrodes[a]

Intensity (W/m^2)	f_{ff}	Efficiency (%)	V_{oc} (V)	I_{sc} (mA/cm^2)
100	0.67 ± 0.01	4.5 ± 0.3	0.66 ± 0.03	1.0 ± 0.1
400	0.58 ± 0.04	4.2 ± 0.1	0.72 ± 0.03	4.0 ± 0.3
700	0.50 ± 0.06	3.5 ± 0.3	0.73 ± 0.01	6.8 ± 0.3
1000	0.47 ± 0.06	3.0 ± 0.4	0.73 ± 0.01	8.6 ± 0.1

[a] Film thickness: 8 μm. The table shows the average values for four electrodes. The light intensity was 100 W/m^2.

Table 2
Compressed electrodes followed by sintering at 450°C for 30 min[a]

Intensity (W/m^2)	f_{ff}	Efficiency (%)	V_{oc} (V)	I_{sc} (mA/cm^2)
100	0.64 ± 0.01	4.3 ± 0.3	0.64 ± 0.01	1.0 ± 0.1
400	0.57 ± 0.02	4.1 ± 0.2	0.69 ± 0.01	4.1 ± 0.3
700	0.52 ± 0.03	3.5 ± 0.2	0.71 ± 0.01	6.6 ± 0.5
1000	0.48 ± 0.04	3.1 ± 0.2	0.72 ± 0.01	9.1 ± 0.8

[a] Film thickness: 8 μm. The table shows the average values for seven electrodes. The light intensity was 100 W/m^2.

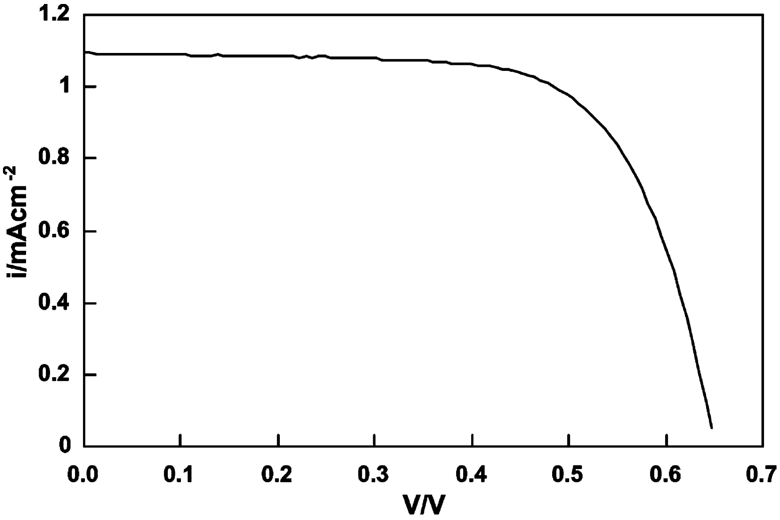

Fig. 3. I–V curve for a 8.3 μm thick TiO_2 film sensitized with N719. The electrode was heated to 120°C for 3 min prior to dye sensitization. The counter electrode was a film of pressed, platinized SnO_2 powder. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2 and 0.5 M *t*-butylpyridine in methoxypropionitrile. Efficiency: 4.9%; f_{ff}: 0.68; V_{oc}: 0.65 V; I_{sc}: 1.1 mA/cm^2; area: 0.19 cm^2; I_{nt}: 100 W/m^2.

shown). The overall conversion efficiency at 1 sun was 2.3%.

In another experiment, an alternative counter electrode was manufactured by pressing a carbon powder mixture on a conducting plastic substrate. The electrode was heated to 120°C for 3 min before use. Fig. 4 displays the I–V curve recorded under indoor illumination conditions (at 230 lx). The fill factor, open-circuit voltage and short-circuit current were 0.59, 0.54 V and 18 μA/cm^2, respectively. These data can be compared to the performance of an amorphous silicon glass module at 250 lx with $f_{\mathrm{ff}} = 0.62$, $V_{\mathrm{oc}} = 0.68$ V and $I_{\mathrm{sc}} = 18\,\mu\mathrm{A/cm}^2$ [6].

3.3. Baseline experiments

Our baseline process is intended to be a reliable state-of-the-art preparation procedure emphasizing control and reproducibility. Fig. 5 displays data extracted from our baseline during 3 months of measurements. The material components are “ITO-60” as plastic substrates supplied by IST (sheet resistance: 60 Ω/square), statically pressed TiO_2 and platinized Sb-doped SnO_2 powders as working and counter electrodes, N719 dye and 0.5 M LiI and 0.05 M I_2 and 0.5 M *t*-butylpyridine in methoxypropionitrile as electrolyte.

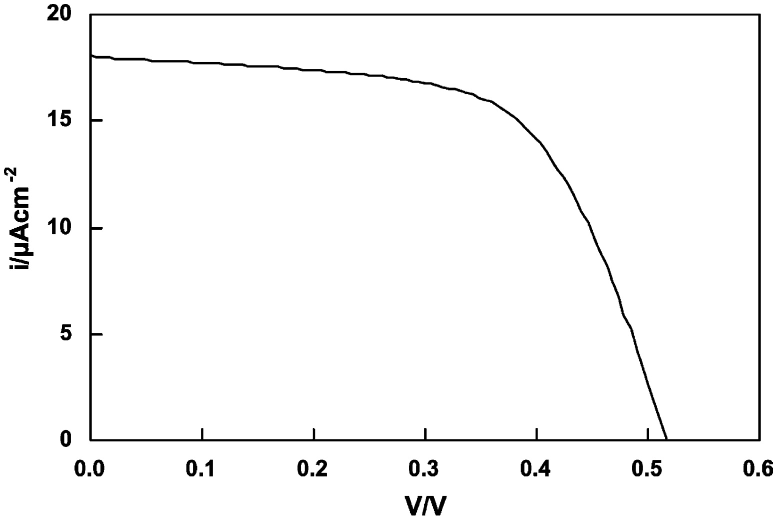

Fig. 4. I–V curve for an 8.3 μm thick TiO_2 film sensitized with N719. The electrode was heated to 120°C for 3 min prior to dye sensitization. The counter electrode was a film of pressed carbon powder on conducting plastic. The electrolyte was composed of 0.5 M LiI, 10 mM I_2 and 0.5 M *t*-butylpyridine in methoxypropionitrile. f_{ff}: 0.59; V_{oc}: 0.54 V; I_{sc}: 18 μA/cm^2; area: 0.39 cm^2; intensity as measured with a black body and a lux meter were 660 μW/cm^2 and 230 lx, respectively.

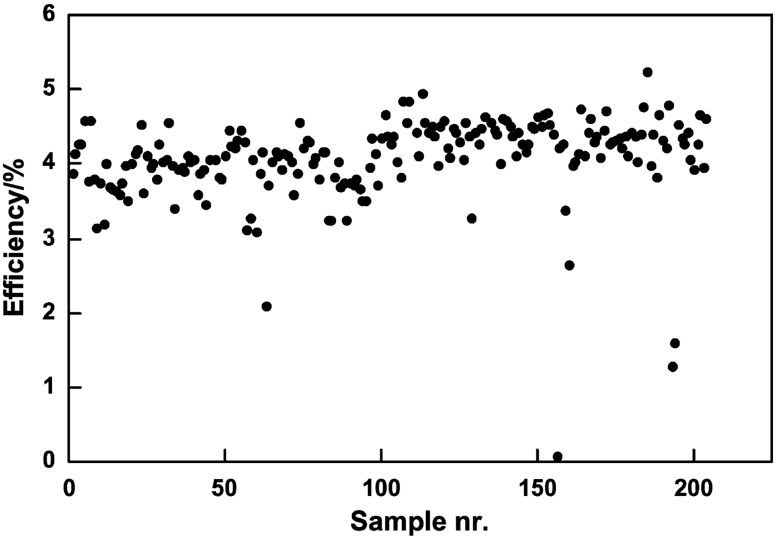

Fig. 5. The accumulated results from our baseline on plastic substrates obtained at a light intensity of 100 W/m^2. The top overall efficiency is around 5.2% and the average efficiency is 4.1 ± 0.4%.

4. Conclusion

We have demonstrated the possibility to make a TiO_2 porous film for a DNSC at room temperature. A press technique is used for the consolidation of the film on glass as well as on flexible substrates.

The mechanical properties and the porosity of the film are very much alike those achieved and measured on control samples made according to the traditional sintering technique regularly used for making the DNSC cells. The photoelectrochemical properties of the pressed DNSC cells are equivalent to those from sintered films.

The press technique offers a much shorter time than sintering for the consolidation of the porous film. The establishment of a static pressure in a press is of the order of seconds compared to heating, sintering and cooling which might take several minutes. In a number of experiments, it is also shown that a flexible porous TiO_2 film can be established by a press nip at a speed of 1 m/s which means a tremendous improvement of production efficiency if such a processing step could be integrated in a continuous production line for DNSC cells.

The press technique opens up possibilities to control the film consolidation process. Primarily the pressure can be varied, which is demonstrated in the present work. Furthermore, the press nip offers the possibility to vary the shape of the press pulse by adjusting the web speed, hardness of the roll surface material as well as the diameter of the roll.

Our vision is to make the DNSC cell competitive to other alternative photovoltaic technologies. This needs much improved production efficiencies and improved solar energy conversion efficiencies than what today state-of-the-art DNSC offers. The press technique, operating at room temperature, offers the possibility to work on flexible substrates which is the basis for a continuous production technique. The press technique also opens up new possibilities to optimize the cell structure in order to enhance the conversion efficiency of solar energy.

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