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Invited feature article

# Low-temperature ozone annealing for dye-sensitized solar cells

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ABSTRACT

The process whereby the $TiO_2$ photoelectrode of dye-sensitized solar cells (DSSCs) is manufactured requires an annealing temperature of 450 °C. However, these DSSCs, which contain a low-cost, lightweight, and flexible plastic substrate, limit the annealing temperature to a maximum of 150 °C. This led us to develop a low-temperature (~150 °C) annealing technique to process the $TiO_2$ photoelectrode. The proposed method, which employs $O_3$ as reactant, is based on the fact that $O_3$ is thermally decomposed at ~150 °C to produce atomic oxygen (O) atoms, to which the $TiO_2$ photoelectrode is then exposed during annealing. Measurement of the carbon contents remaining on the $TiO_2$ photoelectrode using energy dispersive X-ray spectrometry indicated that the O atoms can remove the organic binders contained in $TiO_2$ paste. In addition, measurement of the energy conversion efficiency indicated that O atoms also have the ability to enhance $TiO_2$ interparticle connections. This simple method to supply O atoms may not only be useful for treating the $TiO_2$ photoelectrode of DSSCs but also for other surface treatments that require the use of O atoms.

## 1. Introduction

Since the development of dye-sensitized solar cells (DSSCs) using photoelectrodes consisting of nanoporous $TiO_2$ film by Grätzel et al. [1,2], low-cost solar cells have been researched intensively. Several years ago, Miyasaka *et al*. developed meso-superstructured organometallic halide perovskite solar cells (MSSCs), which attracted widespread attention owing to their high energy conversion efficiency ($\eta$) and affordability [3,4]. However, DSSCs continue to remain an option for low-cost solar cells because MSSCs contain Pb, the use of which is not desirable for safety and environmental reasons, and these cells also have low reproducibility.

The process whereby DSSCs are manufactured requires the $TiO_2$ photoelectrodes to be annealed at temperatures ranging from 450 °C to 550 °C [5]. This annealing process removes the organic binders contained in $TiO_2$ paste and enhances $TiO_2$ interparticle connections, a process known as necking [6]. However, high-temperature annealing can be applied only to DSSCs on glass substrates and is not applicable to DSSCs fabricated using low-cost, lightweight, and flexible plastic substrates because these substrates cannot withstand the high temperature. Although several manufacturing techniques based on low-temperature annealing have been developed for DSSCs with plastic substrates [6–16], DSSCs annealed at low temperature have a much lower $\eta$ value than DSSCs annealed at high temperature [17–22].

In our previous work, we developed a low-temperature (150 °C) annealing technique using ultraviolet (UV) light and dielectric barrier discharge (DBD) to manufacture DSSCs with plastic as well as glass substrates [24]. The reactive oxygen species (ROS) produced by the UV light and DBD remove the organic binders contained in the $TiO_2$ paste and enhance the necking even at low temperature [25]. In addition, the ROS modify the surface of $TiO_2$ films to enable the adsorption of greater amounts of dye, thereby leading to improved $\eta$ values [25]. In the study presented in this paper, we propose an alternative low-temperature ~150 °C method, which is based on $O_3$ annealing and which is an improvement of the low-temperature annealing technique using UV light and DBD. The new method involves the use of an external ozonizer to generate $O_3$, which is allowed to flow into the annealing reactor. In this reactor, atomic oxygen (O), produced by the thermal decomposition of $O_3$, is used for the removal of organic binders and to enhance necking. This method is suitable for mass production batch processing because it obviates the need to install a DBD device or UV lamp in the annealing reactor.

## 2. Experiments

The DSSC samples were prepared as follows. A transparent conductive oxide (TCO) glass substrate (AGC Fabritech, 20 Ω/□, fluorine-doped tin oxide) was used. Although our goal is to manufacture DSSCs

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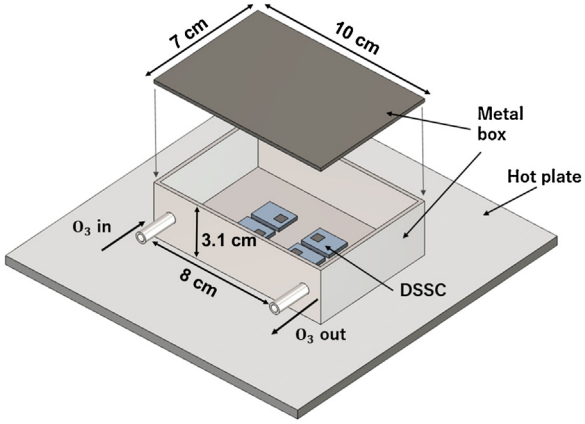


**Fig. 1.** Low-temperature $O_3$ annealing reactor.

with plastic substrates, we used the glass substrate in the present work to eliminate the increase in substrate resistivity due to heating as a result of annealing. Commercially available $TiO_2$ paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was applied to the substrates within an area of 4.7 × 4.7 $mm^2$ by employing screen printing. Fig. 1 shows the low-temperature $O_3$ annealing reactor into which a mixture consisting of $N_2/O_2/O_3$ flows at 500 mL/min. The $O_3$ was generated in a UV-type ozonizer placed far upstream of the reactor. The density of the $O_3$ was varied by changing the ratio of the $N_2/O_2$ mixture flowing into the ozonizer. Four mixtures were used: (1) $N_2/O_2/O_3$ = 0%/100%/1340 ppm, (2) 55%/45%/990 ppm, (3) 80%/20%/570 ppm, and (4) 90%/10%/280 ppm.

The density of each of these $O_3$ mixtures ($[O_3]_{(0)}$) was measured using a UV absorption method before the gas mixture flowed into the reactor. The residence time of the mixture in the reactor was 22 s. After annealing, the samples were immersed in a dye solution (Solaronix N719, 1.9 mM/L in ethanol) for 24 h at 25 °C. Then, glue was used to attach the samples to platinized counter electrodes with spacer sheets, and an electrolyte (Solaronix Iodolyte AN 50) was injected between the substrate and the counter electrode. The average film thickness of the annealed $TiO_2$ films was measured with a stylus profiler (Bruker Corporation, DektakXT-S) and was determined to be 3.1 μm. The ability of the atomic oxygen produced in this manner to eliminate the organic binder was evaluated by measuring the residual carbon contents on the annealed $TiO_2$ films by using energy dispersive X-ray spectrometry (EDX) in combination with scanning electron microscopy (SEM). The extent to which necking was enhanced was evaluated by obtaining the $\eta$ values of the DSSCs from their current–voltage (IV) curves. The IV curves were recorded by using a four-terminal method employing a calibrated xenon lamp (Hamamatsu L2274, 150 W) irradiated at 100 $mW/cm^2$.

## 3. Results and discussion

### 3.1. $O_3$ density and O production rate calculations

In the annealing reactor, $O_3$ is thermally decomposed to produce O and $O_2$ [23]:

$$O_3 + M \rightarrow O + O_2 + M, \quad k_1 = 7.3 \times 10^{-10} \exp\left(\frac{-11400}{T}\right) cm^3/s, \tag{1}$$

where $T$ is the annealing temperature. At the same time, the reverse reaction of (1) also occurs. However, as the reaction coefficient of the reverse reaction is much smaller than $k_1$ in the temperature range of 400-430 K, this reverse reaction can be neglected. The temperatures at the gas inlet and outlet of the reactor and at the surface of the DSSCs were almost the same, as measured with thermocouples; therefore, the temperature in the reactor was assumed to be uniform. The $O_3$ density

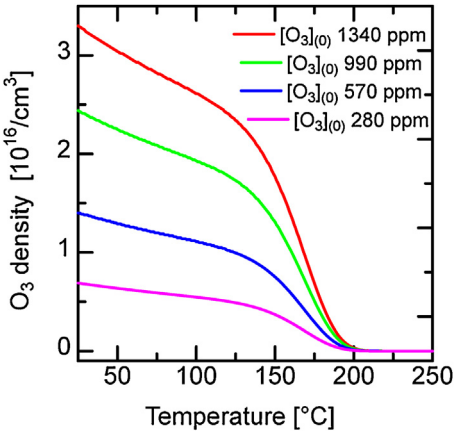


**Fig. 2.** Calculated $O_3$ density near the $TiO_2$ photoelectrodes for temperatures from 25 °C to 250 °C.

($[O_3]$) near the surfaces of the DSSC photoelectrodes, which were positioned approximately at the center of the reactor, is assumed as

$$[O_3] = [O_3]_{(0)} \exp(-k_1 t) \times \frac{298.15}{T}, \tag{2}$$

where $t$ = 11 s (half of the residence time of the mixture). Further, the O production rate ($d[O]/dt$) near the surfaces of the DSSC photoelectrodes is assumed as

$$\frac{d[O]}{dt} = k_1 [O_3][M]. \tag{3}$$

The calculated $[O_3]$ and $d[O]/dt$ for temperatures ranging from 25 °C to 250 °C are shown in Figs. 2 and 3, respectively. Fig. 2 shows that the $[O_3]$ rapidly starts decreasing from 130 °C and becomes approximately 0 at 200 °C. On the other hand, $d[O]/dt$ increases from 100 °C, and decreases after reaching its maximum value at 170 °C. The produced O atoms react with the surfaces of the $TiO_2$ photoelectrodes to remove the organic binder and to enhance necking. The temperature range in which the production rate of O is high (> 130 °C) coincides with the target annealing temperature (at approximately 150 °C). Therefore, the O produced by the thermal decomposition of $O_3$ can be used to treat the $TiO_2$ photoelectrodes at a much lower temperature of ~150 °C than the conventional annealing temperature (450–500 °C).

### 3.2. Residual carbon contents

The residual carbon content on the annealed $TiO_2$ films was measured to evaluate the extent to which the organic binder was removed

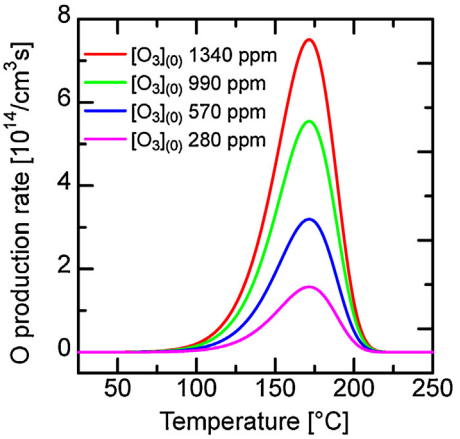


**Fig. 3.** Calculated O production rate near the $TiO_2$ photoelectrodes for temperatures from 25 °C to 250 °C.