Investigation of ultrashort (< 1 min) calcination processes for conversion of Pt–SnO_x from mixture of chloroplatinic acid and tin(II) chloride

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Abstract

We investigate the ultrashort (< 1 min) calcination process for Pt–SnO_x catalysts converted from a mixture solution of chloroplatinic acid and tin(II) chloride in air. An electric furnace is used to test the ultrashort calcination of Pt–SnO_x catalysts used as counter electrodes (CEs) of DSSCs. By using a conventional electric furnace instead of an atmospheric pressure plasma jet (Metals 8:690, 2018), the effect of reactive plasma species can be ruled out, and only the bare thermal effect is considered in this study. Scanning electron microscopy reveals that Pt–SnO_x nanoparticles are well-distributed on the substrates. X-ray photoelectron spectroscopy indicates the conversion of a large amount of metallic Pt and oxidized Sn. No metallic Pt is observed with 5-s calcination; however, ~74% Pt is converted into metallic Pt with 15-s calcination. Further increasing the calcination time does not increase the conversion rate of metallic Pt. By contrast, metallic Sn shows its maximum conversion rate of ~18% with 30-s calcination. Further increasing the calcination time to 30 min reduces the metallic Sn content to ~6%, possibly owing to Sn re-oxidation. When applying Pt–SnO_x catalysts to CEs of DSSCs, the efficiency greatly increases as the calcination time increases from 15 to 30 s. The efficiency remains relatively unchanged for calcination time of 60 s to 30 min. The efficiencies of DSSCs with a Pt–SnO_x CE calcined at longer processing times (≥ 60 s) are comparable to those of DSSCs with conventional Pt CEs.

Graphic abstract The left-hand-side image shows the Pt–SnO_x nanoparticulate compounds. The right-hand-side figure shows the J–V curves.

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1 Introduction

Compounds containing Pt and Sn have been used as electrocatalysts for the counter electrodes (CEs) of dye-sensitized solar cells (DSSCs) [1–9] as well as for applications such as methanol or ethanol oxidation [10], dehydrogenation [11], gas sensing [12–14], 3D electrodes [15], supercapacitors [16], and batteries [17]. Pt is commonly used as a catalyst because of its superior stability and catalytic ability. The addition of a second metal was shown to improve the electrocatalytic reactivity [10, 18]. DSSCs with various types of component materials for CEs, photoanodes, dyes, and electrolytes have been investigated extensively [19–23]. CEs require electrocatalysts for accelerating the reduction from triiodide to iodine (or other redox pairs) and for charge transfer at the electrolyte-CE interface.

Typically a long calcination time (≥ 30 min) is required for the synthesis of catalysts for the CEs of DSSCs [24–30]. This increases the thermal budget and fabrication time in solar cell fabrication processes. We have previously shown that a nitrogen DC-pulse atmospheric pressure plasma jet (APPJ) is an efficient tool for rapidly synthesizing CEs of DSSCs [2, 31]. DSSC efficiency can be improved with APPJ processing for only 5 s. Nitrogen APPJ affords the synergetic effects of reactive plasma species and heat to enable rapid processing of CEs of DSSCs. Reactive nitrogen plasma species possess high energy and chemical reactivity to react with liquid precursors. In this study, we

use a conventional furnace to test the rapid synthesis of Pt-SnO_x nanocompounds that are used as CEs of DSSCs. By comparing the results of this study with those of APPJ-synthesized Pt-SnO_x, we can understand the additional role or reactivity of nitrogen plasma reactive species acting on a mixed liquid precursor consisting of solution of chloroplatinic acid and tin(II) chloride. The ultrashort (< 1 min) calcination of Pt-SnO_x precursors is performed using an electric furnace, and therefore, the effects of reactive plasma species can be ruled out. The results of this study suggest that calcination for 1 min is sufficient to produce Pt-SnO_x catalysts with good electrocatalytic performance. Accordingly, the thermal budget and processing time can be reduced to one-tenth that of the conventional calcination process. The amount of Pt used is also reduced by a factor of two. X-ray photoelectron spectroscopy (XPS) indicates that no metallic Pt remains with 5-s calcination, and $\sim 74\%$ Pt is converted into metallic Pt with 15-s calcination. Further increasing the calcination time does not increase the conversion rate of metallic Pt. By contrast, metallic Sn shows its maximum conversion rate of $\sim 18\%$ with 30-s calcination. Further increasing the calcination time to 30 min reduces the metallic Sn content to $\sim 6\%$, possibly owing to Sn re-oxidation. When using synthesized Pt-SnO_x as CEs of DSSCs, the efficiency significantly improves as the calcination time is increased from 15 to 30 s. The cell performance becomes comparable to that of DSSCs with conventionally processed Pt CEs as the calcination time reaches and exceeds 1 min, indicating the

promising electrocatalytic performance of Pt–SnO_x CEs with ultrashort calcination times.

2 Materials and methods

2.1 Preparation of Pt–SnO_x CEs

The same volume of 25-mM chloroplatinic acid (H₂PtCl₆) (purity 99.95%, Uniregion Biotech) and 25-mM tin(II) chloride (SnCl₂) isopropanol solutions were mixed together and stirred using a magnetic stirrer for 24 h. Then, 60 μl of the H₂PtCl₆–SnCl₂ mixture precursors were spin-coated onto fluorine-doped tin oxide (FTO) substrates for 15 s at 1000 rpm. The samples were then calcined at 510 °C for 5 s, 15 s, 30 s, 60 s, 120 s, 10 min, and 30 min.

2.2 Preparation of TiO₂ photoanodes and DSSC assembly

For the TiO₂ compact layer, the FTO substrates were first spin-coated with a 0.23-M titanium isopropoxide solution and then baked at 200 °C for 10 min. TiO₂ pastes were screen-printed with an area of 0.5 cm × 0.5 cm on the TiO₂ compact layer three times. The detailed procedure for preparing TiO₂ pastes is described in a previous study [2]. Next, TiO₂ photoanodes were calcined at 510 °C for 15 min using a tube furnace. Then, 0.3-mM N719 acetonitrile solution and tertbutyl alcohol mixed in 1:1 volume ratio were used for dye adsorption on TiO₂ mesoporous layers for 24 h.

Sandwich-structure DSSCs were assembled with Pt–SnO_x CEs and TiO₂ photoanodes with a 25-μm-thick spacer. A commercial electrolyte (E-Solar EL 200, Everlight Chemical Industrial Co.) was injected into the CE-photoanode interface to complete the fabrication of the solar cells.

2.3 Characterization of materials and DSSCs

Pt–SnO_x catalysts were inspected by a scanning electron microscope (SEM, JSM-7800F Prime, JEOL). Their chemical bonding status was analyzed by XPS (Thermo K-Alpha, VGS), and the binding energy spectra were fitted using XPSPEAK41 software. To avoid Sn signal interference from FTO substrates, Corning glass substrates were used for samples in the XPS measurement. The binding energy of the C1s core level at 284.6 eV was used to normalize the binding energy. The electrochemical performance of Pt–SnO_x nanocompounds was evaluated by electrochemical impedance spectroscopy (EIS) and Tafel polarization curves using an electrochemical workstation (PGSTAT204, Metrohm-Autolab). Cells with two identical Pt–SnO_x CEs were used for EIS analyses and Tafel measurements. EIS

was performed with 10-mV sinusoidal amplitude from 0.1 to 10⁵ Hz and Tafel measurements were performed from –0.6 to 0.6 V at a scan rate of 50 mV/s. The EIS data were fitted using Z-view software. The DSSC performance was measured using a solar simulator (WXS-155S-L2, WACOM, Saitama, Japan) with an electrometer (Keithley 2440, Tektronix, Beaverton, OR, USA).

3 Results and discussion

Figure 1 shows SEM images of Pt–SnO_x nanoparticles on the FTO substrates. Pt–SnO_x nanoparticles are more likely to distribute in the valley of the FTO grains, possibly owing to the accumulation of the mixture precursor. No significant morphology difference is noted among samples calcined for various durations.

Figure 2a, b show Pt4f and Sn3d spectra for samples calcined for various durations. Tables 1 and 2 respectively show the deconvolution analyses of the binding energy peak areas. The Pt4f spectra include Pt peaks at 71.30 and 74.65 eV, Pt(II) at 72.70 and 76.50 eV, and Pt(IV) at 73.80 and 77.15 eV [32, 33]. The major peaks for 5-s calcination were distributed from Pt(II) and Pt(IV), implying that very little or no amount of metallic Pt was converted from the H₂PtCl₆–SnCl₂ precursor. As the calcination time was increased to 15 s, ~74% of metallic Pt was converted from the precursor. The percentage of converted metallic Pt remained relatively unchanged as the calcination time was increased further. The Pt²⁺ state could be either PtO [34, 35] or Pt(OH)₂ [36]. Figure 2b shows the Sn spectra including Sn(II/IV) and Sn. The binding energy peaks at 485.8 and 494.2 eV were assigned to Sn and those at 487.3 and 495.7 eV [37], to Sn(II/IV). It should be noted that the Sn(II/IV) component is described here instead of Sn(II) and Sn(IV) owing to the small differences between their XPS spectra [38, 39]. It can be observed clearly that Sn(II/IV) dominates the composition of all samples. The conversion rate of metallic Sn increased to 18% as the calcination time was increased from 0 to 30 s. Further increasing the calcination time reduced the metallic Sn content, possibly owing to the re-oxidation of converted metallic Sn. The amount of converted metallic Sn reduced as the calcination time increased from 30 s to 30 min. It is noted that XPS is a surface analysis tool and its results represent only the surface status of the materials. Nevertheless, catalysts are also functioning mainly on the surface. Therefore, the XPS results are still informative in this regard. Further analyses could be done with different take-off angles to gather more information [33].

Figure 3a, b show EIS Nyquist plots of furnace-calcined Pt–SnO_x CEs. The inset of Fig. 3a shows the equivalent circuit [22, 23, 33, 40]. The circuit includes

Fig. 1 SEM images of spin-on $\text{H}_2\text{PtCl}_6\text{-SnCl}_2$ precursors calcined at 510 °C using a tube furnace for various times: **a** 5 s, **b** 15 s, **c** 30 s, **d** 60 s, **e** 120 s, **f** 10 min, and **g** 30 min

series resistance (R_s), charge transfer resistance (R_{ct}), a constant phase element ($\text{CPE1} = (\text{CPE1-T})^{-1} (j\omega)^{-(\text{CPE1-P})}$, where $j = \sqrt{-1}$, ω = frequency), and Warburg impedance ($W1 = (W1-R) \cdot \tanh((j\omega(W1-T))^{W1-P}) \cdot (j\omega(W1-T))^{-(W1-P)}$) [41]. R_s , obtained from the high-frequency intercept on the real axis in the Nyquist plot, indicates the substrate resistance, and R_{ct} , obtained from the radius of the left semi-circle, indicates the charge transfer resistance at the electrode and electrolyte interface [42]. Table 3 shows that R_s remains relatively unchanged in all cases, indicating the comparable resistance of substrates among all samples. R_{ct} of 5-s calcined Pt-SnO_x (3100 Ω) is much higher than those of other samples, suggesting poor electrochemical reactivity. As the calcination time was increased from 15 to 30 s, R_{ct} decreased greatly from 330 to 5.1 Ω , suggesting a major enhancement in electrocatalytic activity. As the calcination time was increased further beyond 60 s, R_{ct} remained low and relatively unchanged; R_{ct} for Pt-SnO_x calcined for 60-s, 120-s, 10-min, and 30-min was 2.2, 1.3, 1.2, and 2.3 Ω , respectively. Lower R_{ct} suggests higher catalytic activities between electrodes and electrolytes [43, 44]. Figure 3c, d show Bode phase plots that can be used to estimate the electron lifetime (τ_e) between electrodes

and electrolytes with $\tau_e = 1/(2\pi f_{\text{peak}})$, where f_{peak} is the peak frequency in the high-frequency region. Table 3 lists the detailed electron lifetimes. The higher peak frequency with shorter electron lifetime indicates that electrons more easily transferred through CEs at the CE-electrolyte interface [45, 46]. The lifetime decreased as the calcination time increased, well-corresponding to the analyses of R_{ct} . A significant decrease in lifetime was noted as the calcination time was increased from 0 to 60 s.

Figure 4 shows Tafel curves tested with symmetric Pt-SnO_x CEs. The Y-axis intercept from the tangential line of the Tafel curve can be described as exchange current density (J_0) [47–49]. J_0 with R_{ct} can also be measured as $J_0 = RT/nFR_{ct}$, where R is the gas constant; T , the temperature; n , the number of electrons involved in the redox reaction; F , the Faraday's constant [50]. The rightmost columns of Table 3 list J_0 estimated using both methods. A larger J_0 is attributed to higher catalytic activity. The J_0 of 5-s calcined Pt-SnO_x CE is 0.0064 mA/cm²; this is much smaller than those obtained from other samples. This suggests poor catalytic activity of 5-s calcined Pt-SnO_x CE. As the calcination time increased, J_0 improved from 0.058 (15-s calcination) to 2.2 mA/cm² (10-min calcination). EIS results

Fig. 2 XPS spectra of **a** Pt4f and **b** Sn3d for samples calcined for various durations

Table 1 Percentage of Pt components obtained from XPS analysis

APPJ Pt4f (%)	Pt 7/2	Pt 5/2	Pt(II) 7/2	Pt(II) 5/2	Pt(IV) 7/2	Pt(IV) 5/2
5 s	—	—	45	40	14	1
15 s	40	34	11	7	3	5
30 s	38	31	9	8	8	6
60 s	37	32	10	8	7	6
120 s	37	31	11	9	7	6
10 min	37	27	11	10	9	6
30 min	35	32	13	10	4	6

and Tafel curves indicated that Pt–SnO_x CEs achieved the highest catalytic ability with 10 min calcination.

Calcined Pt–SnO_x catalysts were used as the CEs of DSSCs. Figure 5 shows the representative current density–voltage (J–V) curves. Figure 6 shows statistics of the solar cell parameters of DSSCs based on six batches

of DSSCs, and Table 4 lists the parameters with standard deviations. The J–V curves indicate a clear enhancement of DSSC performance as the calcination time increases from 15 to 30 s. As the calcination increases to and exceeds 60 s, the power conversion efficiencies (PCEs) become nearly constant; the PCEs of DSSCs with 60-s, 120-s,

Table 2 Percentage of Sn components obtained from XPS analysis

APPJ Sn3d (%)	Sn 5/2	Sn 3/2	Sn(II/IV) 5/2	Sn(II/IV) 3/2
5 s	3	Trace	57	40
15 s	5	3	54	38
30 s	12	6	48	34
60 s	6	2	54	38
120 s	5	1	55	39
10 min	5	2	55	38
30 min	4	2	56	38

10-min, and 30-min calcined Pt-SnO_x CEs are $4.31 \pm 0.30\%$, $4.47 \pm 0.33\%$, $4.44 \pm 0.22\%$, and $4.42 \pm 0.28\%$, respectively. As the calcination time increases from 5 to 60 s, major improvements are seen in the fill factor (FF) and photocurrent density (J_{sc}), and a slight improvement is seen in the open circuit voltage (V_{oc}). The low solar cell efficiencies

in 5-s and 15-s calcined samples well correspond to the analyses based on EIS and Tafel measurements. XPS results indicate that ~74% of metallic Pt was converted with 15-s calcination; however, the performance of DSSC with 15-s calcined Pt-SnO_x remained poor. Nonetheless, the analyses of EIS and Tafel experiments showed that significant improvements indeed occurred as the calcination time increased from 15 to 30 s. We speculate that a slightly longer calcination time after the catalysts have been converted may be required to improve the adhesion between the converted Pt-SnO_x catalysts and the glass substrate. This could enhance the charge transfer and electrocatalytic effect of the calcined Pt-SnO_x. In comparison to our previous study of APPJ-calcined Pt-SnO_x with a liquid precursor film prepared in a similar manner [31], the APPJ process can improve DSSC efficiency in a shorter processing time (5 s). This could possibly be attributed to the plasma effect in addition to heat contributing to this material

Fig. 3 **a** Nyquist curves of the symmetric cells with two identical Pt-SnO_x CEs; inset image of **a** is the equivalent circuit diagram for fitting. **b** Locally magnified plot of **a**. **c** Bode phase plots of the symmetric cells with two equal Pt-SnO_x CEs. **d** Locally magnified plot of **c**

Table 3 EIS parameters of Pt-SnO_x CEs

Counter electrode	R _s (Ω)	R _{ct} (Ω)	CPE1-T (μF/cm ²)	CPE1-P	W1			τ _e (μs)	J ₀ ^a (mA/cm ²)	J ₀ ^b (mA/cm ²)
					W1-R(Ω)	W1-T(s)	W1-P			
Pt–SnO _x Furnace										
5 s	22	3100	8.98	0.93	2400	1200	0.5	2004	0.0041	0.0064
15 s	19	330	16	0.87	2100	1700	0.5	634	0.039	0.058
30 s	19	5.1	98	0.86	2.5	2.5	0.5	100	2.4	1.6
60 s	19	2.2	130	0.77	2.6	3.0	0.5	80	5.9	1.9
120 s	19	1.3	190	0.73	2.6	3.2	0.5	40	10	2.0
10 min	17	1.2	190	0.74	2.6	4.8	0.5	32	11	2.2
30 min	19	2.3	130	0.76	3.6	2.3	0.5	45	5.7	1.7

^a J_0 : exchange current density is calculated from R_{ct} ^b J_0 : exchange current density is calculated from Tafel curve **Fig. 4** Tafel measurement of symmetric cells with various Pt-SnO_x CEs **Fig. 5** Representative J-V curves of DSSCs with Pt-SnO_x CEs calcined for various durations

conversion process. A similar synergetic effect of reactive plasma species and heat could also be found with APPI processing of Pt-reduced graphene oxide composite materials [4]. For typical electrodeposition of Ni-Pt compound CEs of DSSCs, the required processing time is 1 h [25, 26]; further, for typical spin-casting and drop-casting of Ni-Co compounds, the required processing time is 30 min [27, 28].

4 Conclusions

Ultrashort (< 1 min) calcination processes for Pt-SnO_x catalysts converted from a mixture solution of chloroplatinic acid and tin(II) chloride are investigated and compared with longer calcination times of 2, 10, and 30 min. XPS indicates the conversion of a large amount of metallic Pt and oxidized Sn. No metallic Pt is observed with 5-s calcination; however, ~ 74% Pt is converted into metallic Pt as the calcination time increases to 15 s. At calcination times exceeding 15 s, the metallic Pt concentration remains relatively unchanged. Metallic Sn shows its maximum conversion rate of ~ 18% with 30-s calcination. Further increasing the calcination time to 30 min reduces the metallic Sn content to ~ 6%, possibly owing to Sn re-oxidation. The EIS and Tafel measurement results also indicate a significant improvement in the electrocatalytic effect as the calcination time increases from 15 to 30 s. However, when Pt-SnO_x catalysts are used as CEs of DSSCs, the cell efficiency remains poor for the case with 15-s calcination despite the fact that ~ 74% metallic of Pt has been converted. We suspect that a slightly longer calcination time is required for better adhesion between the converted Pt-SnO_x catalysts and the glass substrate for improved electrocatalytic effects.

Fig. 6 Statistics of solar cell parameters based on six different batches of DSSCs

Table 4 Solar cell parameters for DSSCs with Pt-SnO_x CEs calcined for various durations

Condition	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
Pt	0.70 ± 0.01	10.17 ± 0.45	61.33 ± 0.44	4.35 ± 0.23
Pt-SnO _x furnace				
5 s	0.68 ± 0.03	2.94 ± 0.11	8.87 ± 0.82	0.18 ± 0.02
15 s	0.66 ± 0.04	3.38 ± 1.50	13.05 ± 4.05	0.33 ± 0.30
30 s	0.69 ± 0.00	10.06 ± 0.20	53.48 ± 3.40	3.69 ± 0.22
60 s	0.70 ± 0.01	10.40 ± 0.90	59.59 ± 1.29	4.31 ± 0.30
120 s	0.70 ± 0.01	10.44 ± 0.80	61.39 ± 0.64	4.47 ± 0.33
10 min	0.71 ± 0.01	10.33 ± 0.49	60.97 ± 1.80	4.44 ± 0.22
30 min	0.70 ± 0.01	10.17 ± 0.81	62.06 ± 0.94	4.42 ± 0.28

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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