Low-Temperature Chemical Sintered TiO₂ Photoanodes Based on a Binary Liquid Mixture for Flexible Dye-Sensitized Solar Cells

Md. Mahbubur Rahman¹, Hyeong Cheol Kang², Kicheon Yoo², and Jae-Joon Lee²*
¹Department of Applied Chemistry, Konkuk University, Chungju 27478, Korea
²Department of Energy Materials Science and Engineering, Research Center for Photoenergy Harvesting & Conversion Technology (phct), Dongguk University, Seoul 04620, Korea

ABSTRACT
A chemically sintered and binder-free paste of TiO₂ nanoparticles (NPs) was prepared using a binary-liquid mixture of 1-octanol and CCl₄. The 1:1 (v/v) complex of CCl₄ and 1-octanol easily interacted chemically with the TiO₂ NPs and induced the formation of a highly viscous paste. The as-prepared binary-liquid paste (PBL)-based TiO₂ film exhibited the complete removal of the binary-liquid and residuals with the subsequent low-temperature sintering (~150ºC) and UV-O₃ treatment. This facilitated the fabrication of TiO₂ photoanodes for flexible dye-sensitized solar cells (f-DSSCs). For comparison purposes, pure 1-octanol-based TiO₂ paste (PO) with moderate viscosity was prepared. The PBL-based TiO₂ film exhibited strong adhesion and high mechanical stability with the conducting oxide coated glass and plastic substrates compared to the PO-based film. The corresponding low-temperature sintered PBL-based f-DSSC showed a power conversion efficiency (PCE) of 3.5%, while it was 2.0% for PO-based f-DSSC. The PBL-based low- and high-temperature (500ºC) sintered glass-based rigid DSSCs exhibited the PCE of 6.0 and 6.3%, respectively, while this value was 7.1% for a 500ºC sintered rigid DSSC based on a commercial (or conventional) paste.

Keywords: Dye-sensitized solar cells, Raoult’s law, Binder-free TiO₂ paste, 1-Octanol, Carbon tetrachloride, Low-temperature, High viscosity

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1. Introduction
Since the invention of dye-sensitized solar cells (DSSCs) in 1991, extensive research has been performed to understand the operation principle and improve the power conversion efficiency (PCE) [1-3]. As a consequence, the PCE of over 14% was achieved for conventional glass/fluorine-doped tin oxide (FTO) substrate and high-temperature (500ºC) sintered TiO₂ photoanode-based rigid DSSCs (g-DSSCs) [4,5]. The fabrication of TiO₂ photoanodes under low-temperature (150ºC or lower temperature range) sintering conditions for DSSCs application has attracted substantial interest over the conventional high-temperature sintering process. This is advantageous not only for the fabrication cost reduction but also for developing mobile power sources for wearable electronic and IoT devices with lightweight and flexibility [6,7]. Additionally, the low-temperature fabrication method can be applicable for preparing multilayer structures with different dyes at each layer that can facilitate the PCE enhancement by solar spectrum splitting in the course of light passage through the photoanode [8].

The preparation of TiO₂ photoanodes for conventional high-efficiency g-DSSCs fabrication requires the use of organic binders such as polyethylene glycol, ethylcellulose, and hydroxypropyl cellulose. These binders increase the viscosity of the TiO₂ pastes and enable the preparation of highly stable, crack-free, and homogenous mesoporous TiO₂ (mp-TiO₂) films with a thickness of t > 10 µm [9,10]. During the sintering process at 500ºC, these organic binders are burned out and facilitate the formation of mp-TiO₂ layers. In addition, this process induces the
development of excellent electrical pathways for transporting photo-injected electrons by improving the interparticle connection of TiO$_2$ and the adhesion of the TiO$_2$ layer with glass/FTO substrates [9-11]. However, the conventional binder containing TiO$_2$ pastes and the high-temperature sintering methods are unsuitable for fabricating transparent conducting oxide-coated plastic substrates-based flexible DSSC (f-DSSC) [8]. This is because flexible plastic substrates, indium tin oxide/polyethylene naphthalate (ITO/PEN) and ITO/polyethylene terephthalate (ITO/PET), cannot withstand a process at a temperature exceeding 150ºC [12].

So far, mechanical pressing [13,14], electrophoretic deposition [15-17], microwave sintering [18], spray-deposition [19], chemical sintering [20,21], and film transfer (lift-off) [22] methods have been demonstrated for fabricating low-temperature processed TiO$_2$ film onto the flexible substrates for DSSCs application. Among these methods, mechanical methods for TiO$_2$ film fabrication required complicated multi-step fabrication processes with additional post-treatment, and they were generally ineffective for preparing a TiO$_2$ film with a thickness of > 10 µm [7]. Additionally, these TiO$_2$ film fabrication methods result in imperfect TiO$_2$ NPs interconnections and poor adhesion of the TiO$_2$ film with the flexible plastic substrates, resulting in inefficient charge transfer and collection in f-DSSCs [7,23].

Contrary to the mechanical methods, the solution-processed chemical sintering approach is promising for fabricating low-temperature sintered TiO$_2$ pastes and the corresponding TiO$_2$ films onto flexible plastic substrates with reduced fabrication steps, low cost, and high enough film thickness [21,23]. Furthermore, the chemical sintering approach offers the advantages of large-scale production of TiO$_2$ film with improved mechanical stability [23]. Accordingly, chemical sintering approaches were reported to prepare binder-free TiO$_2$ pastes using nano-glue (5 nm TiO$_2$ particles), ethanol, ammonia, acid-base mixture, acids, and water [21,23-26].

Park et al. developed a binder-free TiO$_2$ paste using acid-base chemistry of CH$_3$COO$^-$ and NH$_4^+$ in solution [21]. The flocculation formation of TiO$_2$ nanoparticles (NPs) induced by CH$_3$COO$^-$ and NH$_4^+$ could enhance the viscosity by improving the interaction between the TiO$_2$ NPs. The resulting binder-free and chemically sintered TiO$_2$ photoanode exhibited a PCE of 2.55% in g-DSSCs [21]. In another report, Li et al. developed a nano-glue-based TiO$_2$ paste with a well-interconnected NPs network [23]. The nano-glue acts as a chemical sintering agent for TiO$_2$ NPs, in which the ample surface hydroxyl groups (-OH) of nano-glue are well mixed with the TiO$_2$ NPs and increase the viscosity of the paste. The corresponding low-temperature sintered DSSC, fabricated with a plastic substrate-based TiO$_2$ photoanode and a platiniized glass/FTO substrate-based counter electrode (CE), exhibited a PCE of 5.43%.

Strong acids such as hexa-fluorotitanic acid (H$_2$TiF$_6$) and hydrochloric acid (HCl) were used for preparing low-temperature chemically sintered TiO$_2$ pastes for f-DSSCs [25,26]. The oxidizing nature of acids can increase the amounts of -OH groups on the TiO$_2$ surface and improve the TiO$_2$ interparticle connection with the subsequent dehydration reaction at the low-temperature sintering conditions. Holliman et al. prepared a low-temperature sintered TiO$_2$ paste using H$_2$SiF$_6$ as a chemical sintering agent with a PCE of 4.2% in DSSC based on ITO/PET photoanode substrate and glass/FTO based CE substrate [26]. In another report, Weerasinghe et al. used HCl as a chemical sintering agent for preparing TiO$_2$ film with a PCE of 5% in f-DSSC [26]. Although these acids pastes-based TiO$_2$ films showed good adhesion with the substrates, the possible chemical etching of the ITO and FTO conducting layer by the H$_2$TiF$_6$ and HCl can lower the fill factor (FF) and photocurrent of the DSSCs devices [26]. Therefore, it is essential to develop ITO and FTO corrosion-resistant TiO$_2$ pastes, which exhibit high enough viscosity with sufficient mechanical strength and thickness of the TiO$_2$ layers and strong adhesion to the conductive flexible plastic substrates after low-temperature sintering.

In this study, a novel binary-liquid mixture of carbon tetrachloride (CCl$_4$) and 1-octanol was used for preparing chemically sintered low-temperature TiO$_2$ paste for f-DSSCs. The unfavorable physical and chemical properties of CCl$_4$, including high volatility, low-boiling temperature ($T_b$ = 76.72°C), and low viscosity (0.965 cP), were not suitable for the preparation of TiO$_2$ pastes. Thus, 1-octanol with high $T_b$ (194.5°C) and high-viscosity (7.36 cP) was introduced into the CCl$_4$ for preparing highly viscous, binder-free, and chemically and low-temperature sintered TiO$_2$ pastes. According to Raoult’s law [27], the high $T_b$ of 1-octanol could decrease by the low $T_b$ of...
CCl₄ and facilitate the preparation of TiO₂ films sintered at low temperature (≤150°C). The formation of the 1-octanol-CCl₄ complex could easily interact with the TiO₂ NPs via hydrogen bonding. This induced the reduction of TiO₂ interparticle distance and enabled the preparation of high-viscous pastes. The as-prepared chemically sintered and low-temperature TiO₂ films exhibited good inter-particle connection and porosity, improved mechanical strength, and strong adhesion to the ITO/PEN and glass/FTO substrates. The 150°C sintered g-DSSCs and f-DSSCs fabricated with this binary-liquid paste exhibited PCEs of 6.0 and 3.5%, respectively.

2. Experimental

2.1 Chemicals and reagents

All the reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA). Cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719) dye was purchased from Solaronix, Switzerland. ITO/PEN (13 Ω/sq.) and glass/FTO (8 Ω/sq.) were purchased from Pecell Technologies Inc (Japan) and Pilkington (USA), respectively.

2.2 Preparation of the TiO₂ pastes

Before preparing the TiO₂ pastes, the TiO₂ powder (Degussa P25) was pre-treated with acetylacetone to minimize NPs aggregation [9]. Then, 1 g of pre-treated TiO₂ powder was mixed with two compositions of 1-octanol and CCl₄ (1:1 and 1:0 (v/v)) and stirred at room temperature (RT) for 6 h. Subsequently, the mixture was homogenized for another 30 min to obtain homogenous dispersion of TiO₂ NPs by using an ultrasonic horn. The mixture was heated again at 70°C with stirring (300 rpm/s) for 24 h to obtain the high viscous pastes. The pastes were denoted hereafter as P₁₀ and P₀, where the composition of 1-octanol and CCl₄ were 1:1 and 1:0 (v/v), respectively.

2.3 Fabrication of DSSCs devices

The as-prepared TiO₂ pastes were coated on flexible ITO/PEN and glass/FTO substrates by the doctor blade method and dried at RT. Then, the TiO₂ films were sintered at 150°C for 60 min in an electric oven in the presence of air. Subsequently, the films were treated with UV-O₃ for 30 min. For comparison, the P₈ and a commercial binder containing TiO₂ paste (P₉) (TTPH-20N, ENBKOREA Co., Ltd., Korea, particle size 20 nm) were used to prepare 500°C sintered TiO₂ films on glass/FTO substrate according to a previously reported method [28]. The thickness of the P₁₀ and P₀-based TiO₂ films was ca. 15.8 and 15.3 µm, respectively, while it was ca. 15.4 µm for P₉-based TiO₂ photoanode. All the TiO₂ electrodes were dipped into the N719 dye solution (0.3 mM) in ethanol for 18 h. For the preparation of f-DSSCs CE, Pt was sputtered on ITO/PEN substrate for about 10 s. While for the preparation of g-DSSCs CEs, 5 mM chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) solution in ethanol was drop cast onto the glass/FTO substrate and sintered in an electric muffle furnace at 400°C for 20 min in air. The dye-loaded photoelectrodes (active area ca. 0.25 cm²) and Pt-CEs were sandwiched using 60-µm thick Surlin film (Solaronix SA, Switzerland) as a spacer and sealing agent using a hot press. The electrolyte solution with the composition of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.1 M I₂, and 0.5 M 4-tert-butylpyridine (tBP) and 1 mM 4′,6-diamidino-2-phenylindole (DAPI) as an efficient energy relay dye (ERD) [29] were dissolved in 3-methoxypropionitrile (MPN) and injected into the cells through the drilled holes on the CEs. The holes were sealed by using surlin film with cover glass.

2.4 Instrumentations

The viscosity of the TiO₂ pastes was measured with a viscometer (µVisc, Rheosense, Inc., USA). The thickness of the TiO₂ films was measured by a surface profilometer (Accretech, Japan), and the adhesion of TiO₂ film with FTO was evaluated by a scotch-tape scratch test. The strength of adhesion of the films was evaluated using a peel-off tester (Top-Tac 2000, Korea). The crystallographic pattern of TiO₂ was characterized with an X-ray diffractometer (XRD, Philips, X’pert, Netherland) and enabled the preparation of high-viscous pastes. The as-prepared chemically sintered and low-temperature TiO₂ films exhibited this binary-liquid paste exhibited PCEs of 6.0 and 3.5%, respectively.

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measured using a UV−Vis absorption spectrophotometer (Perkin-Elmer Lambda 35). A solar simulator (Polaronix® K201, McScience, Korea) with a 200 W Xenon lamp with the incident light intensity of 100 mW/cm² (AM 1.5 G) was used for the photovoltaic (PV) measurements of the DSSCs. A PV power meter (Polaronix® K101 LAB20, McScience, Korea) was used to measure the current density-voltage (J-V) characteristics of DSSCs. A PV power meter (Polaronix® K101 LAB20, McScience, Korea) was used to measure the current density-voltage (J-V) characteristics of DSSCs. Incident photon-to-electron conversion efficiency (IPCE) spectra were obtained by an IPCE measurement system (Polaronix, K3100 Spectral IPCE, McScience) with a 300 W xenon lamp source. Electrochemical impedance spectra (EIS) were measured using an impedance analyzer (IM6ex, Zahner Zahner-Elektrik GmbH & Co. KG, Germany) in the frequency range from 10⁵ to 0.1 Hz with the ac amplitude of 5 mV under open-circuit potential and dark conditions. The EIS spectra were analyzed with an appropriate equivalent circuit using Z-view software (Scribner Associates Inc., version 3.1). Thermogravimetric (TGA) analyses were performed with a Scinco TGA-N 1000 analyzer (Seoul, Korea) under ambient atmospheric conditions.

3. Results and Discussion

3.1. Mechanism of TiO₂ NPs interconnection

Fig. S1 presents the bar diagram of the Tₓ variation of the CCl₄ and 1-octanol mixture against their volume fraction. The Tₓ of the binary mixture was increased by increasing the volume fraction of 1-octanol that is in accordance with Raoult’s law [27]. Considering the preparation of binder-free, low-temperature chemically sintered TiO₂ paste, and the composition of CCl₄ and 1-octanol complex formation [30], a 1:1 volume ratio is selected as the optimized composition, where the Tₓ of 1-octanol:CCl₄ (1:1 v/v) was 97°C. The schematic illustration of the TiO₂ NPs inter-connections in the mp-TiO₂ film based on Pₒ is presented in Scheme 1. In the mixture of 1-octanol, CCl₄, and TiO₂ NPs, 1-octanol and CCl₄ could easily form a complex with a 1:1 (v/v) ratio via hydrogen bonding (O-H·····C1-C) [30]. Subsequently, this complex could interact with the -OH groups on the TiO₂ NPs surface and form Ti-O-C-O-C₈H₁₇ and Ti-O-C-O-Ti bonds by the elimination of HCl. This enabled to decrease in the TiO₂ interparticle distance and formed a viscous paste. In the subsequent heat treatment of the as-prepared TiO₂ NPs film at 150°C, CO₂ and H₂O can be eliminated by the decomposition of hydrocarbon chains and the dehydration of -OH groups on the surfaces of TiO₂ NPs, respectively. This induces to interconnect the TiO₂ NPs through the Ti-O-C-O-Ti bonds. Finally, upon the UV-O₃ treatment, Ti-O-C-O-Ti bonds can be broken and the residual carbon can be eliminated in the form of CO₂ and O₂ [31], resulting in the further reduction of TiO₂ interparticle distance and forming a highly stable mp-TiO₂ network through Ti-O-Ti bonds. This induces the decoloring of the film, which can be attributed to the complete removal of the remaining organic residues, as shown in Fig. S2. Meanwhile, for the case of Pₒ, TiO₂ NPs are homogeneously distributed into the 1-octanol due to the physical adsorption as well as the hydrogen bonding interaction between the -OH groups of TiO₂ and 1-octanol. Upon heat treatment of the as-prepared Pₒ-based TiO₂ film at 150°C, 1-octanol can effectively bridge the gap between TiO₂ NPs by dehydration process. Finally, in the UV-O₃ treatment, the residual 1-octanol and carbon can be eliminated as CO₂ and O₂ (Fig. S2), thus, facilitating the formation of TiO₂ film with moderate stability.

![Scheme 1. Schematic illustrations of the TiO₂ interparticle connection in binary liquid-based TiO₂ paste via a dehydration process at 150°C and subsequent UV-O₃ treatment.](image)
3.2. Rheological behaviors

Fig. 1a shows the viscosity of the TiO$_2$ pastes (P$_{BL}$, P$_O$, and P$_C$) and the maximum strength of their corresponding TiO$_2$ films prepared onto the glass/FTO substrates by the doctor blade method. The corresponding photo-image of P$_{BL}$ and P$_O$ pastes is presented in Fig. 1b. The rheological behavior of the TiO$_2$ pastes revealed that the addition of CCl$_4$ with 1-octanol significantly increased the viscosity of the TiO$_2$ paste from 38,214 (P$_O$) to 53,158 (P$_{BL}$) cPs. This can be attributed to the hydrogen bonding between the TiO$_2$ NPs and the complex of CCl$_4$ and 1-octanol [30,32], which concurrently increase the maximum strength of adhesion of the 150°C sintered TiO$_2$ film from 192 (P$_O$) to 229 (P$_{BL}$) gf/mm$^2$. These values were 98245 cPs and 282 gf/mm$^2$ for P$_C$ under 500°C sintering conditions. These results are consistent with the tape test results for the mechanical adhesion of P$_{BL}$ compared to P$_O$ (Fig. S3) on a glass/FTO substrate upon sintering at 150°C followed by subsequent UV-O$_3$ treatment. P$_{BL}$ showed the highest level of adhesion without affecting the cross-cut areas (~0%), while P$_O$ exhibited a much lower degree of adhesion by detaching the cross-cut areas of ~10%.

3.3. Morphological, TGA, and XRD analyses

The morphology of TiO$_2$ films prepared from the P$_{BL}$ and P$_O$ was studied with FE-SEM. The TiO$_2$ film of P$_{BL}$, before heat treatment at 150°C, exhibited crack-free homogenous distribution of TiO$_2$ NPs with a relatively homogenous distribution of particle aggregation (Fig. S4a). In contrast, the TiO$_2$ film of P$_O$ showed some cracks over the TiO$_2$ film with an enhanced particle aggregation by forming bigger local clusters over the film (Fig. S4b). After sintering at 150°C and subsequent UV-O$_3$ treatment, the TiO$_2$ film of P$_{BL}$ showed high porosity without the presence of NPs aggregation (Fig. 2a), while the TiO$_2$ film of P$_O$ exhibited lower porosity with the presence of bigger local clusters over the film (Fig. 2b). The carbon content in the TiO$_2$ film of P$_{BL}$ was analyzed by EDS under different treatment conditions (e.g., drying at 25°C, 150°C, 150°C followed by UV-O$_3$ treatment, and 500°C), as shown in Fig. 2c. The corresponding EDS spectra are presented in Fig. S5. It was observed that the carbon content in P$_{BL}$ decreased significantly after both sintering at 150°C and subsequent UV-O$_3$ treatment with a carbon content of 1.76%. This value for the RT dried and 150°C sintered P$_{BL}$-based TiO$_2$ films was 3.0 and 2.48%, respectively. Further, a small reduction of the carbon content at 500°C sintering condition (1.47 wt%) evidently showed that the additional UV-O$_3$ treatment is very critical to eliminating the carbon residues after sintering at relatively low temperatures. The thermogram in Fig. 2d exhibited a continuous weight loss up to 62 and 51.75%, respectively, for P$_{BL}$ and P$_O$ at 138°C, while no further significant weight loss was observed until 500°C (63.50 and 53.15%, respectively, for P$_{BL}$ and P$_O$), consistent with the previous weight loss data. The little high residual percentage of P$_O$ compared to P$_{BL}$ can be ascribed to the incomplete removal of 1-octanol from P$_O$ induced by its high T$_b$ (194.5°C). These results demonstrated that both P$_{BL}$ and P$_O$ pastes are suitable for the preparation of binder-free $n$-DSSCs photoanodes under low-temperature sintering conditions with subsequent UV-O$_3$ treatment. Additionally, the crystallographic pattern of the TiO$_2$ NPs in the P$_{BL}$ and P$_O$-based TiO$_2$
films exhibited that anatase is the major crystal phase (JCPDS card no. 21-1272) (Fig. S6) [33]. This is advantageous for improved dye-loading and the development of high-performance DSSCs [34].

3.4. Photovoltaic characterizations

Fig. 3a presents the photo-current density-voltage (J-V) plots of the g-DSSCs based on the TiO₂ photoanodes of PBL and PO, sintered at 150°C. The resulting PV parameters are summarized in Table 1. It was observed that the PO cell showed the lowest PV performance with the short-circuit current density (Jₛₑ), open-circuit potential (Vₒ𝑐), and PCE of 8.45 mA/cm², 0.73 V, and 4.2%, respectively. Meanwhile, the PBL cell exhibited the PCE enhancement of 30% compared to the PO cell with the Jₛₑ, Vₒ𝑐, and PCE of 12.07 mA/cm², 0.73 V, and 6.0%, respectively. The increase in the PCE of PBL cell compared to the PO device is mostly due to the increase in Jₛₑ. This can be attributed to the improved dye loading in PBL (2.51 × 10⁻⁸ mol/cm²) compared to the PO (ca. 1.8 × 10⁻⁸ mol/cm²) (Fig. S7a). The high visible transparency of the TiO₂ film of PBL compared to the PO film (Fig. S7b) is another possible reason for increased Jₛₑ. Meanwhile, the 500°C sintered PBL-based g-DSSC exhibited a PCE of 6.3%, which is comparable to the PCE of PC cell (7.10%) (Fig. 3b and Table 1). The improved PV performance of the Pc-based g-DSSCs is due to the enhanced TiO₂ interparticle connection compared to PBL, which corroborates a 24.32% higher Jₛₑ. This result suggests that PBL is promising to develop conventional high-temperature sintered g-DSSCs.

Finally, f-DSSCs were fabricated by utilizing PBL and PO on ITO/PEN substrate, and the resulting J-V plots and PV parameters are summarized in Fig. 3c and Table 1, respectively. Similar to the g-DSSCs, the fully flexible cell with PBL exhibited a PCE of 3.5% with the Jₛₑ, Vₒ𝑐, and FF of 9.42 mA/cm², 0.70 V, and
52.3%, respectively, while the PCE was 2.0% for $P_O$ with the $J_{sc}$, $V_{oc}$, and FF of 6.42 mA/cm$^2$, 0.68 V, and 46.8%, respectively. By inspection, the 75% PCE enhancement for $P_{BL}$-based f-DSSC compared to the $P_O$ device is mainly due to the significant increase of $J_{sc}$ (46.72% enhancement). This can be attributed to the improved TiO$_2$ interparticle connection and dye loading of the $P_{BL}$-based TiO$_2$ film compared to the TiO$_2$ film based on $P_O$. Nevertheless, The PCE of the $P_{BL}$-based f-DSSC is 71.40% lower than the g-DSSC prepared under similar conditions. This can be ascribed to the high ohmic resistance of the ITO/PEN substrate as well as the internal resistance of the devices, which corroborated a significantly low FF. The PCE of the $P_{BL}$ DSSC is higher or comparable to the previously reported g-DSSCs and f-DSSCs prepared under low-temperature sintering conditions (Table S1), suggesting that $P_{BL}$ can be effectively uti-
lized for developing high-performance DSSCs with additional electrode engineering. Fig. 3d shows the IPCE spectra of the corresponding f-DSSCs based on P_{BL} and P_{O}. It can be observed that the external quantum efficiency (EQE) of the P_{BL} cell exhibited an upward shift over the wide wavelength range (400–800 nm) with the maximum EQE value of 54% at 540 nm, while this value for the P_{O} device was 41% at 540 nm. This result is consistent with the J_{sc} values of the corresponding f-DSSCs devices.

3.5. Electrochemical characterizations

EIS spectra of the P_{BL} and P_{O}-based f-DSSCs were measured to investigate the electron transport mechanism and the interfacial properties. Fig. 4 shows the EIS spectra of the devices in the form of Nyquist plots, which exhibited three semicircles. The semicircle at the high-, mid-, and low-frequency regions corresponds to the charge transfer resistance at the CE/electrolyte interface (R_{ct}), charge transfer resistance at the TiO_{2}/dye/electrolyte interface (R_{ct2}), and the diffusion resistance (Z_{diffusion}) within the electrolyte, respectively [35]. The intercept with the real axis at the high-frequency region corresponds to the contact resistance (R_{c}) between the TiO_{2}/substrate or the ohmic resistance of the cells [35,36]. Generally, the R_{c} values do not alter much in a DSSC with similar substrates and paste. However, a little lower R_{c} for the P_{BL} cell (13.2 W) than the P_{O}-based f-DSSC (14.4 W) suggests the lower contact resistance between the P_{BL} TiO_{2} film and ITO/PEN substrates. This can be attributed to the strong adhesion of the P_{BL} TiO_{2} film with the substrate [36], consistent with the scotch tape and mechanical adhesion tests. The R_{ct} values for P_{BL} and P_{O} devices are 21.36 and 27.49 W, respectively. The lower R_{ct2} designates the faster interfacial charge transfer process and lower recombination in the P_{BL} device compared to the P_{O} device [35], which is consistent with the PV parameters of their corresponding f-DSSC.

4. Conclusions

This study described the utilization of 1-octanol with high viscosity and high T_{b} together with CCl_{4} with low viscosity and low T_{b} to prepare a binder-free TiO_{2} paste for low-temperature sintered f-DSSCs. The 1:1 (v/v) complex of CCl_{4} and 1-octanol could interact with the TiO_{2} NPs via hydrogen bonding, which reduced the TiO_{2} interparticle distance and formed a vicious TiO_{2} paste. This binary-liquid-based TiO_{2} paste, P_{BL}, exhibited strong adhesion to the FTO/glass and ITO/PEN substrates with high mechanical stability. The P_{BL}-based f-DSSC and g-DSSC, sintered at 150 and 500ºC, respectively, exhibited PCEs of 3.5 and 6.3%, respectively. The PCE for f-DSSC and g-DSSC based on pure 1-octanol paste and sintered at 150ºC, were 2.0 and 4.0%, respectively, while this value for commercial 500ºC sintered P_{C}-based g-DSSC was 7.1%. The significantly improved PCE of P_{BL}-based f-DSSC and g-DSSC compared to the pure 1-octanol paste-based cells can be attributed to the strong adhesion and high mechanical stability of the corresponding TiO_{2} film with improved porosity and dye loading. This result demonstrated the applicability of the P_{BL} paste for the development of both low- and high-temperature sintered DSSCs. We strongly believe that the present methodology is promising for developing high-efficiency f-DSSCs by choosing other highly viscous alcohols and low boiling temperature liquids.

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Supporting information

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