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### Short communication

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#### ABSTRACT

In this study, binary ionic liquids (bi-IL) of imidazolium salts containing cations with different carbon side chain lengths (C = 2, 4, 6, 8) and anions such as iodide (I<sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>), hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) and trifluoromethansulfonate (SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>) were used as electrolytes in dye-sensitized solar cells (DSSCs). On increasing the side chain length of imidazolinium salts, the diffusion coefficients of I<sub>3</sub><sup>-</sup> and the cell conversion efficiencies decreased; however, the electron lifetimes in TiO<sub>2</sub> electrode increased. As for different anions, the cell which contains 1-butyl-3-methyl imidazolium trifluoromethansulfonate (BMISO<sub>3</sub>CF<sub>3</sub>) electrolyte has better performance than those containing BMIBF<sub>4</sub> and BMIPF<sub>6</sub>. From the impedance measurement, the cell containing BMISO<sub>3</sub>CF<sub>3</sub> electrolyte has a small charge transfer resistance ( $R_{ct2}$ ) at the TiO<sub>2</sub>/dye/electrolyte interface. Moreover, the characteristic frequency peak for TiO<sub>2</sub> in the cell based on BMISO<sub>3</sub>CF<sub>3</sub> is less than that of BMIBF<sub>4</sub> and BMIPF<sub>6</sub>, indicating the cell with bi-IL electrolyte based on BMISO<sub>3</sub>CF<sub>3</sub> has higher electron lifetime in TiO<sub>2</sub> electrode. Finally, the solid-state composite was introduced to form solid-state electrolytes for highly efficient DSSCs with a conversion efficiency of 4.83% under illumination of 100 mW cm<sup>-2</sup>. The long-term stability of DSSCs with a solidified bi-IL electrolyte containing SiO<sub>2</sub> nanoparticles, which is superior to that of a bi-IL electrolyte alone, was also presented.

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### 1. Introduction

Because of the possible low production cost and the expected high energy conversion efficiency, dye-sensitized solar cells (DSSCs) with nanocrystalline TiO<sub>2</sub>, organic dyes and electrolytes become a large scale prevalent material for light harvesting [1]. These solar cells usually employ liquid electrolytes containing  $I^-/I_3^-$  redox couple as supporting electrolyte in order to reduce the dye cation, generated by the injection of the photo-excited electron. A few additives were usually added into the electrolyte to improve the open-circuit voltage ( $V_{OC}$ ). However, as far as long-term stability of the solar cell is concerned, use of the liquid electrolytes must be avoided since the organic solvents evaporate slowly leading to decrease in cell performance. Hence, in order to improve the long-term stability of DSSCs, some efforts were made to replace the organic solvent electrolytes, such as polymer electrolytes [2], organic hole-transport materials [3] and inorganic semiconductors [4], but their conversion efficiency are relatively low due to the imperfect contact between the dye anchored electrode and the hole conductor. Ionic liquids (ILs) based electrolytes are a promising alternative electrolyte to DSSCs because of their intriguing properties such as negligible vapor pressure and non-flammability [5–8].

In this study, we compare the physicochemical properties of different structures of ILs such as 1-alkyl-3-methylimidazolium tetrafluoroborate containing various alkyl side chain lengths (alkyl chains used having the chemical formula  $C_nH_{2n+1}$ ,where n=2, 4, 6, 8), and 1-butyl-3-methylimidazolium salts containing various anions such as  $BF_4^-$ ,  $PF_6^-$  and  $SO_3CF_3^-$  on the cell performance at room temperature (25 °C). The influence of solidified electrolyte with SiO<sub>2</sub> nanoparticles was also investigated.

Electrochemical impedance spectroscopy (EIS), a steady-state method measuring the current response to the application of an ac voltage as a function of the frequency [9], has been widely employed to study the kinetics of electrochemical and photoelectrochemical processes including the elucidation of salient electronic and ionic process occurring in the DSSCs [10]. In this study, we use EIS for the analysis of charge transport resistances in DSSCs, and further fit the curves in Nyquist plot and calculate the exact time constant of the electrons in DSSCs, so as to understand the effect of various ILs in DSSCs.

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#### $R_{ct2}(\Omega)$ Ionic liquid $D_{app}$ (I<sup>-</sup>) (cm<sup>2</sup> s<sup>-1</sup>) $D_{app}$ (I<sub>3</sub><sup>-</sup>) (cm<sup>2</sup> s<sup>-1</sup>) $J_{SC}$ (mA cm<sup>-2</sup>) $V_{\rm OC}(V)$ η(%) FF $R_{diff}(\Omega)$ $\tau_n \,(\mathrm{ms})^{\mathbf{b}}$ $4.40 imes 10^{-7}$ $2.01 imes 10^{-7}$ 7.78 23.8 45.2 12.3 **EMIBF**₄ 0.647 2.98 0.597 BMIBF<sub>4</sub> $3.64\times10^{-7}$ $1.36 \times 10^{-7}$ 0.651 3.02 581 777 0 5 9 2 249 12.5 $2.98\times10^{-7}$ $1.04\times10^{-7}$ HMIBF₄ 7.51 0.643 2.81 0.582 27.7 63.4 14.4 OMIBF<sub>4</sub> $2.71\times10^{-7}$ $1.02\times10^{-7}$ 0.529 26.8 70.3 22.9 7.46 0.651 2.57 BMIPF<sub>6</sub> $3.18\times10^{-7}$ $1.20 \times 10^{-7}$ 6.76 0.649 2.61 0.596 23.2 60.2 12.7 $3.58\times10^{-7}$ $1.31\times10^{-7}$ 0.615 15 5 BMISO<sub>3</sub>CF<sub>3</sub> 10 18 0.657 4 11 575 201

Table 1 The photovoltaic and EIS parameters of the DSSCs based on biionic liquids with various side chain lengths and anions. The ion diffusion coefficients were calculated from the limiting currents measured by 10 μm Pt ultramicroelectrode.<sup>a</sup>

<sup>a</sup> All data were measured at ca. 25 °C.

<sup>b</sup> The values of  $\tau_n$  were calculated from the fitting data of EIS measurements.

#### 2. Experimental

#### 2.1. Materials

Anhydrous iodine, poly(ethylene glycol) (PEG, MW = 20,000), tertiary butanol and 4-tertiary butyl pyridine (TBP) were obtained from Merck and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>), 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIBF<sub>4</sub>), 1-octyl-3-methylimidazolium tetrafluoroborate 1-butyl-3-methylimidazolium hexafluorophosphate  $(OMIBF_4),$  $(BMIPF_6),$ 1-butyl-3-methylimidazolium trifluoromethansulfonate (BMISO<sub>3</sub>CF<sub>3</sub>), and titanium (IV) isopropoxide (TTIP) were obtained from Acros and used without further purification. The SiO<sub>2</sub> nanoparticle (Aesoil 200, ca. 12 nm) was received from Degussa Company. The cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) (N3 dye) was purchased from Solaronix (Aubonne, Switzerland).

#### 2.2. Preparation of dyed-TiO<sub>2</sub> electrode

The TiO<sub>2</sub> paste was prepared by sol–gel process in acid medium by autoclaving of TTIP that concentrated to 13 wt% at 240 °C for 12 h [11] in which 30 wt% PEG was added to prevent the film cracking during drying. The TiO<sub>2</sub> paste was coated on a fluorine-doped tin oxide (FTO) glass ( $R_{\rm sh}$  = 15  $\Omega$  square<sup>-1</sup>) using glass rod and the electrodes were sintered at 500 °C for 30 min. An active area of 0.25 cm<sup>2</sup> was selected from sintered electrode and then immersing in 3 × 10<sup>-4</sup> M solution of N3 dye dissolved in acetonitrile and tertiary butanol mixture (1/1, v/v) for 12 h.

#### 2.3. The assembly and characterization of the DSSCs

The bi-IL electrolytes are obtained by mixing BMII with EMIBF<sub>4</sub>, BMIBF<sub>4</sub>, HMIBF<sub>4</sub>, OMIBF<sub>4</sub>, BMIPF<sub>6</sub>, or BMISO<sub>3</sub>CF<sub>3</sub> (13/7, v/v), respectively, followed by addition of 0.2 M I<sub>2</sub> and 0.5 M TBP. Pt (100 nm thick) sputtered on FTO was used as the counter electrode. The cell was fabricated by keeping a 25- $\mu$ m ionomer resin (Surlyn 1702, Dupont, USA) between the two electrodes with the electrolyte in between. The electrolytes were injected into the gap between the electrodes by capillarity, and the injecting process was kept at 80 °C because the viscosity of the IL electrolyte at 80 °C was low enough to penetrate into the space. The electrolyte-injecting hole was made with a drilling machine, and the hole was sealed with hot-melt glue. When the high viscous electrolytes were used, filling of the electrolyte into the cells was not always successful. Therefore, the performances of DSSCs reported in this study were based on the average values from three samples.

The DSSCs were energized by using a light source of 450 W Xe lamp (#6266, Oriel) equipped with a water-based IR filter and AM 1.5 filter (#81075, Oriel). Photoelectrochemical characteristics and the EIS measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie) under

illumination of 100 mW cm<sup>-2</sup> and in the dark with applied bias from -0.5 to -0.7 V. The applied voltage and ac amplitude were set at  $V_{\rm OC}$  of the DSSCs or various biases and 10 mV, respectively, in the frequency range 10 mHz to 65 kHz. The impedance spectra were analyzed by an equivalent circuit model [12]. A two-electrode electrochemical cell, consisting of a 10- $\mu$ m radius Pt ultramicroelectrode as working electrode and a Pt foil as counter electrode, was used to measure the diffusion coefficients of iodide and triiodide.

#### 3. Results and discussions

# 3.1. Electrochemical measurement of the apparent diffusion coefficient

The rate of recombination of injected electron with oxidized dye is considered as one of the important factors controlling the photocurrent of the DSSCs. To avoid the current loss, regeneration of the dyes by electron donor, I<sup>-</sup>, has to be sufficiently fast to interrupt the back reaction, where the diffusivity of I<sup>-</sup> and I<sub>3</sub><sup>-</sup> play important roles. The apparent diffusion coefficients ( $D_{app}$ ) of I<sup>-</sup> and I<sub>3</sub><sup>-</sup> can be calculated from anodic and cathodic steady-state currents by ultramicroelectrode technique using the equation:

$$I_{ss} = 4ncaFD_{app} \tag{1}$$

where *n* is the number of electron transferred, *F* is the Faraday constant, *a* is the radius of ultramicroelectrode and *c* is the bulk concentration of electroactive species [13]. Steady-state voltammograms for  $I^-/I_3^-$  in 1-alkyl-3-methylimidazolium tetrafluoroborate with various lengths of side chain (C=2, 4, 6, 8) and BMI<sup>+</sup> with different anions were investigated and the calculated  $D_{app}$  are shown in Table 1. The result shows that the  $D_{app}$  of  $I^-$  and  $I_3^-$  decrease from  $4.40 \times 10^{-7}$  to  $2.71 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> and  $2.01 \times 10^{-7}$  to  $1.02 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, respectively, by increasing the side chain length of ILs from C2 to C8. On the other hand, BMI<sup>+</sup> containing BF<sub>4</sub><sup>-</sup> has higher  $D_{app}$  than PF<sub>6</sub><sup>-</sup> or SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>. The  $D_{app}$  results show an inverse trend to the viscosity of the ILs.

In Fig. 1, the  $D_{app}$  of I<sup>-</sup> was also measured with various volume percentage of BMII in BMISO<sub>3</sub>CF<sub>3</sub>, and that increases from  $0.18 \times 10^{-7}$  to  $2.75 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> by lowering the BMII from 100 to 10%. The apparent discrepancy in the variation of viscosity and diffusion coefficient of I<sup>-</sup> has been rationalized by the Dahms–Ruff equation [14,15].

$$D_{app} = D_{phys} + D_E = D_{phys} + \frac{k_{EX}\delta^2 c}{6}$$
(2)

where  $D_{phys}$ , diffusion coefficient,  $D_E$ , electron exchange diffusion coefficient,  $k_{EX}$ , rate constant of electron exchange, c, concentration and  $\delta$ , average center-to-center distances between redox species. The  $D_E$  term behaves in a different manner from the viscositydependant  $D_{phys}$  term. The high packing density of I<sup>-</sup> favors a Grotthus-type exchange mechanism, leading to a higher  $D_E$  [16],



**Fig. 1.** (a) Steady-state voltammograms of a 10- $\mu$ m radius of Pt ultramicroelectrode in the binary mixture ionic liquids of BMII and BMISO<sub>3</sub>CF<sub>3</sub>. BMII volume percentages: (1) 10%, (2) 20%, (3) 40%, (4) 60%, (5) 80% and (6) 100%. (b) The dependence of steadystate current and diffusion coefficient of I<sup>-</sup> on the volume percentage of BMII.

and this can be illustrated as follows:

$$I_3^- + I^- \to I^- \dots I_2 \dots I^- \to I^- + I_3^-$$
 (3)

Zistler et al. also suggested that the transport behavior of  $I_3^-$  in binary IL system (MPII-BMIBF<sub>4</sub> blends) does not obey the Einstein–Stokes equation [17].

#### 3.2. Photovoltaic parameters and EIS analysis on DSSCs

The photovoltaic characteristic parameters of DSSCs based on different ILs are also listed in Table 1. The DSSC containing EMIBF<sub>4</sub> has higher current density and conversion efficiency than other chain lengths due to higher  $D_{app}$  of I<sup>-</sup> and I<sub>3</sub><sup>-</sup>. The charge transport in DSSCs was determined by the transport of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> in the IL electrolytes, thus the decreased fill factor (FF) and cell conversion efficiency with the increase of the side chain length.

Fig. 2(a) and (b) shows the Nyquist plots of EIS of the DSSCs containing IL with different side chain lengths and anions, respectively, measured under 100 mW cm<sup>-2</sup>. The equivalent circuit is shown as the inset of Fig. 2(a). All the spectra exhibit three semicircles, which are assigned to electrochemical reaction at Pt/electrolyte, charge transfer at the TiO<sub>2</sub>/dye/electrode and Warburg diffusion process of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> in the electrolyte. The equivalent circuit employed for the curves fitted the impedance spectra of the DSSCs are also shown in Table 1. The  $R_{diff}$  increased with the increase in the side chain length, and the similar trend has been observed with the  $D_{app}$  also.



**Fig. 2.** Impedance spectra of the DSSCs containing various ionic liquids measured at  $V_{OC}$ , 100 mW cm<sup>-2</sup>: (a) Nyquist plots of DSSCs based on ionic liquids with different side chain length [inset: the equivalent circuit]. (b) Nyquist plots of DSSCs based on ionic liquids with different anions. (c) Bode phase plots of DSSCs based on ionic liquids with different anions.

Meanwhile, the time constant  $(\tau_n)$  can be obtained via Eq. (4)

$$\tau_n = R_{ct2} \times C_{\mu 2} \tag{4}$$

where  $R_{ct2}$  and  $C_{\mu 2}$  are the charge transfer resistance and the chemical capacitance at TiO<sub>2</sub>/dye/electrolyte interface, respectively. The chemical capacitance ( $C_{\mu 2}$ ) is an equilibrium property that relates the variation of the carrier density to the displacement of the Fermi level. The  $C_{\mu 2}$  is a positive quantity, as it represents the equilibrium property. The time constant of electron in TiO<sub>2</sub> film increases from 12.3 to 22.9 ms with the increase in side chain length from C2 to C8. This result is similar to the previously reported results by Kubo et al. [18], where the electron lifetimes increase with increasing of side chain length of imidazolium iodides from C3 to C9. Thus, it was found that the DSSC containing C7-imidazolium iodides has the best conversion efficiency due to the combination effects of the electron lifetime in TiO<sub>2</sub> electrode and the electrolyte viscosity [18]. In our study, as listed in Table 1, the DSSC containing EMIBF<sub>4</sub> has higher current density and cell conversion efficiency than other longer side chain lengths. Meanwhile, the FF significantly decreased with the increase in side chain length, which was due to the increase in ions diffusion resistance and the lower electron transfer at the counter electrode. It is supported via the high-frequency  $(10^3 - 10^5 \text{ Hz})$  peaks in the Bode phase plot shift to lower frequency with increasing of side chain length (not shown here). Consequently, the electron lifetime in TiO<sub>2</sub> electrode and the viscosity of electrolyte are the two main effects on the cell performances of DSSCs with bi-IL electrolyte systems.

As to the effects of anions of ionic liquids on DSSCs, the  $R_{diff}$  values and the time constants of the BMIBF<sub>4</sub>, BMIPF<sub>6</sub> and BMISO<sub>3</sub>CF<sub>3</sub> based DSSCs are found to be 8.03, 11.99, 7.71  $\Omega$  and 12.5, 12.7, 20.1 ms, respectively, as also shown in Table 1. Besides, Fig. 2(c) shows that the corresponding characteristic frequency peaks (1–10<sup>3</sup> Hz) of BMISO<sub>3</sub>CF<sub>3</sub> is smaller than that of BMIBF<sub>4</sub> and BMIPF<sub>6</sub>. Thus, the DSSC containing BMISO<sub>3</sub>CF<sub>3</sub> has smaller  $R_{diff}$  and longer electron lifetime, which resulted in the best cell performance, in which the short-circuit current ( $J_{SC}$ ), open-circuit voltage ( $V_{OC}$ ), conversion efficiency ( $\eta$ ) and FF were 10.18 mA cm<sup>-2</sup>, 0.657 V, 4.11% and 0.615, respectively, as listed in Table 1.

The DSSCs are also measured by EIS in the dark to elucidate correlation of the electron transport at TiO<sub>2</sub>/electrolyte interface with anions of ionic liquids are shown in Fig. 3. In DSSCs, the electrons are transported through the mesoscopic TiO<sub>2</sub> network and react with  $I_3^-$ . The reduced I<sup>-</sup> ions are oxidized to  $I_3^-$  at the counter electrode simultaneously. So, the net current of a cell is largely dependent on the applied bias. It is found that the BMISO<sub>3</sub>CF<sub>3</sub> based cell has higher resistance than that based on others. By giving larger bias, the difference becomes larger for the three ILs (Fig. 3(a)). This means that the DSSC based on BMISO<sub>3</sub>CF<sub>3</sub> system has less recombination and higher  $V_{OC}$ . Also, the cell containing BMISO<sub>3</sub>CF<sub>3</sub> has larger time constant due to slower recapture of conduction band electrons by  $I_3^-$ , which is shown in Fig. 3(b).

# 3.3. Influence of SiO<sub>2</sub> nanoparticles in the biionic liquid electrolytes

Due to the high viscosity of IL, a slower mass transport is expected and the diffusion of redox couple will dominate the performance of DSSCs. Recently, a relative improvement of the ILs based DSSCs were reported, in which the nanoparticles were added and solidified the electrolyte [19,20]. The order of the electrolyte structure is beneficial for the electron hoping. Herein, we also study the influence of SiO<sub>2</sub> nanoparticles on the charge transport in the electrolyte.

Charge transport between two Pt coated electrodes in a symmetric cell could be described by the limiting current density ( $J_{LIM}$ ) [21]. The  $J_{LIM}$  and the  $D_{app}$  of  $I_3^-$  in IL electrolytes with various amounts of nano-SiO<sub>2</sub> are shown in Fig. 4(a). The addition of SiO<sub>2</sub> nanoparticles in IL electrolyte obviously increased both  $J_{LIM}$  and  $D_{app}$  of  $I_3^-$  and satisfied at 4 wt%. However, the further increase leads to the decrease of the  $J_{LIM}$  and the  $D_{app}$  of  $I_3^-$ . The performances of DSSCs revealed that the  $J_{SC}$  and cell conversion efficiency increase to 11.3 mA cm<sup>-2</sup> and 4.83%, respectively, by adding SiO<sub>2</sub> nanoparticles



**Fig. 3.** (a) Electron transport resistance at the  $TiO_2$  electrode/electrolyte interface and (b) time constant based on ionic liquid with different anions fitted and calculated from EIS measured in the dark and applied biases from -0.5 to -0.7 V.

at 4 wt%, as shown in Fig. 4(b). The enhancements in  $J_{SC}$  and  $\eta$  were 13 and 17%, respectively, when compared with the electrolyte without containing SiO<sub>2</sub> nanoparticles. As to the EIS measurement, the values of  $R_{diff}$  of electrolytes significantly decrease from 0 to 4 wt%, and have little increase from 6 to 8 wt%, which is in accordance with the results of  $J_{LIM}$ . In addition, the  $J_{SC}$  was always lower than  $J_{LIM}$  due to the electron recombination at the TiO<sub>2</sub>/dye/electrolyte interface, which may lower the  $J_{SC}$  at such high iodine concentration (0.2 M of I<sub>2</sub>).

# 3.4. The durability test of the solidified DSSCs based on biionic liquid electrolytes

As shown in Fig. 5, the bi-IL electrolyte containing  $4 \text{ wt\% SiO}_2$  achieved better durability over a period of 576 h, as compared to that without adding SiO<sub>2</sub>. In this experiment, the overall power conversion efficiency was measured once each day after being stored in the dark at room temperature. Interestingly, the overall power conversion efficiency of the DSSC with  $4 \text{ wt\% SiO}_2$  nanoparticles in the bi-IL electrolyte increased ca. 5%, and that of the DSSC without adding SiO<sub>2</sub> nanoparticles in the bi-IL electrolyte decreased ca. 5% after being stored for more than 576 h. Those results suggest that the addition of  $4 \text{ wt\% SiO}_2$  in bi-IL electrolyte could improve the stability of DSSC. This study has provided a useful technique for fabricating dye-sensitized solar cells with no loss in their intrinsic performance.



**Fig. 4.** (a) The limiting current density ( $J_{LLM}$ ) and the  $D_{app}$  of  $I_3^-$  of IL electrolytes and (b) the short-circuit current densities ( $J_{SC}$ ), cell conversion efficiencies ( $\eta$ ) of DSSCs, and ion diffusion resistance ( $R_{diff}$ ) fitted from Nyquist plots, with various amounts of SiO<sub>2</sub> nanoparticles in electrolytes measured under illumination of 100 mW cm<sup>-2</sup> and 25 °C.



Fig. 5. The at-rest durability data of the DSSCs based on bi-IL electrolyte with/without  $SiO_2$  nanoparticles.

#### 4. Conclusion

We have investigated the non-solvent based biionic liquid electrolyte systems applied on the DSSCs. The performances of cells fabricated with various ILs were evaluated according to the photocurrent density-voltage characteristics and the EIS analyses. The ion diffusion coefficients and conductivities of electrolytes, and cell efficiencies decrease with the increase in side chain length: vice versa for the electron lifetime in TiO<sub>2</sub> electrode was observed. Furthermore, comparing the cell performances with different anions, the device made with electrolyte containing BMISO<sub>3</sub>CF<sub>3</sub> has better cell performance than those containing BMIBF<sub>4</sub> and BMIPF<sub>6</sub>. According to the EIS measured at 100 mW cm<sup>-2</sup>, the cell based on BMISO<sub>3</sub>CF<sub>3</sub> has a small  $R_{ct2}$ , although the  $R_{diff}$  was similar to that containing BMIBF<sub>4</sub>. Finally, the solid-state DSSC based on bi-IL with 4 wt% SiO<sub>2</sub> nanoparticles exhibited an encouraging conversion efficiency of 4.83% under illumination of 100 mW cm<sup>-2</sup> (AM 1.5G). Moreover, the durability test concluded that the addition of 4 wt% SiO<sub>2</sub> in bi-IL electrolyte could improve the stability of the DSSC.

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