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A Multi-Electron Transporting Layer for Efficient Perovskite Solar Cells

Kritsada Hongsith ^{1,2,3}, Vasan Yarangsi ^{1,2,3}, Sukrit Sucharitakul ^{1,2,3}, Surachet Phadungdhithada ^{1,2,3}, Athipong Ngamjarurojana ^{1,2,3} and Supab Choopun ^{1,2,3,*}

¹ Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand; kritsada354@gmail.com (K.H.); vasan.yarangsi@gmail.com (V.Y.); sukrit.sucharitakul@cmu.ac.th (S.S.); surelity@gmail.com (S.P.); ngamjarurojana@yahoo.com (A.N.)

² Research Center in Physics and Astronomy, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

³ Thailand Center of Excellence in Physics, Ministry of Higher Education, Science, Research and Innovation, 328 Si Ayutthaya Road, Bangkok 10400, Thailand

* Correspondence: supab99@gmail.com; Tel.: +66-819-512-669

Abstract: In this work, a multi-electron transporting layer (ETL) for efficient perovskite solar cells is investigated. The multi-ETL consists of five conditions including SnO_2 , $\text{SnO}_2/\text{SnO}_x$, TiO_2 , $\text{TiO}_2/\text{SnO}_2$, and $\text{TiO}_2/\text{SnO}_2/\text{SnO}_x$. The best performance of PSC devices is found in the $\text{SnO}_2/\text{SnO}_x$ double-layer and exhibits a power conversion efficiency equal to 18.39% higher than the device with a TiO_2 single-layer of 14.57%. This enhancement in efficiency can be attributed to a decrease in charge transport resistance (R_{ct}) and an increase in charge recombination resistance (R_{rec}). In addition, R_{ct} and R_{rec} can be used to explain the comparable power conversion efficiency (PCE) between a PSC with a $\text{SnO}_2/\text{SnO}_x$ double-layer and a PSC with a triple-layer, which is due to the compensation effect of R_{ct} and R_{rec} parameters. Therefore, R_{ct} and R_{rec} are good parameters to explain the efficiency enhancement in PSC. Thus, the R_{ct} and R_{rec} from the electrochemical impedance spectroscopy (EIS) technique is an easy and alternative way to obtain information to understand and characterize the multi-ETL on PSC.

Keywords: perovskite solar cell; charge transfer resistance; electrochemical impedance spectroscopy; electron transporting layer; multi-layer

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1. Introduction

Recently, the perovskite solar cell (PSC), as a new type of solar cell, has become an excellent photoelectric converter due to its low-cost and high-efficiency ability to harvest solar energy [1–7]. Currently, the efficiency of perovskite solar cells has increased up to 25.5% [8]. Typically, the structure of a perovskite solar cell mainly consists of three parts: an electron transporting layer (ETL), a perovskite layer, and a hole transporting layer (HTL). Recently, metal oxide wide-band-gap semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), etc., have gained attraction for PSC applications as the charge transporting layer [9–14]. This is because of their high mobility, good energy alignment, and use of low-temperature processes [15–17]. However, the energy conversion efficiency of PSCs using metal oxide is quite volatile, due to the effect of many factors that depend on the structure of PSCs, such as morphology or thickness of metal oxide in the charge transporting layer [18–20]. Thus, many techniques have been used to investigate and study the charge transport resistance (R_{ct}) and charge recombination resistance (R_{rec}) of PSCs with metal oxide in the charge transporting layer. One of the interesting techniques is electrochemical impedance spectroscopy (EIS).

EIS is one of the techniques for characterizing the electrical properties of materials and interfaces with conducting electrodes. This technique has been widely used to obtain

information of carrier dynamical processes in the interfaces of layers [21–24]. EIS is a frequency-domain measurement method using the application of a small sinusoidal AC perturbation. The impedance measurements are recorded as a wide frequency sweep at a single disturbance amplitude. The most common spectral representations are impedance spectra, namely Nyquist and Bode plots. The resistor and capacitor results are separated by EIS according to process kinetics. In the Nyquist diagram, the complex negative segments are plotted against the real portion of the impedance, with the frequency as an implicit variable. This technique has been applied with relative success in the perovskite solar cells field because multiple effects occur simultaneously.

This EIS measurement technique is generally applied to study electron transporting layers. For example, H. Yi et al. [25] modified the electron transporting layer by using SnO₂ nanoparticles, sol–gel SnO₂, and bilayer SnO₂. From the results, the bilayer SnO₂ devices showed the highest efficiency compared with the reference single-layer device. The increase in PCE can be explained by decreases in current leakage, higher electron transfer, and trap state in interfacial recombination. For the EIS results, the bilayer SnO₂ PSC showed a lower charge transfer resistance explained by increasing charge extraction phenomena from perovskite to ETL. A. R. Pascoe et al. [26] have studied impedance spectroscopy in planar PSC devices through the characterization of cells by employing a variety of constituent layers. Comparing the characteristic EIS time constants with time-resolved photoluminescence and open-circuit voltage decay, this work provides an empirical basis for understanding the impedance spectrum in planar PSCs.

In this work, a multi-electron transporting layer for efficient perovskite solar cells is investigated. The multi-layer ETL is composed of a TiO₂ compact layer, a SnO₂ layer, and is covered by a thin-film SnO_x layer by the sputtering method. The enhancement in efficiency is discussed in terms of charge transfer resistance, charge recombination resistance, and electron lifetime in PSCs that can be simply derived from EIS spectra.

2. Experimental Details

2.1. Multi-ETL Preparation

The multi-ETL was prepared in the following manner. First, the glass substrate was used and the fluorine-doped tin oxide (FTO) was patterned using zinc powder and a solution of hydrochloric acid (HCl) and deionized (DI) water mixtures. Next, the FTO substrate was cleaned using a solution of detergents (Alconox). After that the solution was changed using DI water, acetone, and isopropanol, each in 15 min, respectively, and all solutions were placed in a sonicator machine. After that, the FTO glass substrate was dried using nitrogen gas. Next, treatment on the surface of the FTO glass substrate was completed using UV ozone cleaner for 15 min. Then, the multi-ETL was modified; a sequential step for the multi-ETL is summarized in Figure 1a. The TiO₂ compact (CP) layer was prepared using titanium diisopropoxide bis (acetylacetonate) in absolute ethanol at a volumetric ratio of 1:7. The FTO substrate was coated with the mixture solution using spin coating deposition at 6000 rpm for spin speed for 30 s and annealed at 500 °C for 1 h. SnO₂ films were prepared by using a precursor solution of SnCl₂·2H₂O in ethanol (0.1 M) at 4000 rpm 30 s by spin coating and was annealed at 180 °C for 1 h. Finally, the SnO_x layer was coated using the DC magnetron sputtering technique at a power of 60 W for 5 s and annealed at 180 °C for 1 h.

Figure 1. Schematic diagram of: (a) modified sequential thickness of ETL, (b) structure, and (c) energy band diagram of n-i-p perovskite solar cell.

2.2. Device Fabrication

The perovskite solutions were prepared in the following manner. First, the mixed cation halide perovskite layer was prepared using concentration for 1.1 M of lead iodide (PbI_2), 1 M of Formamidinium iodide (FAI), 0.02 M of methylammonium bromide (MABr), 0.075 M of cesium iodide (CsI), and 0.22 M of lead (II) bromide (PbBr_2). All materials were mixed in a solution of DMF and DMSO at a 4:1 volume ratio and the last step was stirring at 70 °C for 2 h. The hole transporting layer (HTL) using the Spiro-OMeTAD solution was prepared similarly to our previous work [27] by mixing Spiro-OMeTAD 72 mg, 4-tert-butyl pyridine 28.8 μL , and Li-TFSI solution 17.5 μL (Li-TFSI 520 mg in 1 mL of anhydrous acetonitrile) in 1 mL of chlorobenzene (CB).

The device's structure and principle of perovskite solar cell consisting of (FTO/ETL/Perovskite/Spiro-OMeTAD/Ag) are shown in Figure 1b,c. The numbers in Figure 1c represent the energy level of conduction and valence band in each layer obtained from [27,28]. The perovskite layer was prepared using a one-step deposition method in a homemade nitrogen glove box with a controlled relative humidity of about RH 10% at room temperature used for preparing perovskite films. The perovskite solution was dropped on ETL by two-step spin rate. The first spin rate was 1000 rpm for 10 s and the second step was 4000 rpm for 25 s. For the second spin rate, 350 μL of chlorobenzene was dropped as an antisolvent to remove excess perovskite solution. After that, the device was annealed at 100 °C for 40 min and cooled down to room temperature. Later, the layer of HTL was prepared using Spiro-OMeTAD precursor solution covered on the perovskite layer using a spin coating technique for 4000 rpm for 30 s. Lastly, the top of the device was coated with the Ag films for back contact of PSC using thermal evaporation.

The thickness of the ETL is an important parameter for PSC performance. The thickness on this work is applied based on our previous work and other reported work [27,28]. The thickness of SnO_2 is about 145 nm, SnO_x is about 10 nm, and TiO_2 is in the order of 50 nm.

2.3. Characterization of Films and Device

For the measurement of the photovoltaic characteristics of PSC, we used a solar light simulation of 100 mW/cm^2 (AM1.5) with an Ossila Solar Cell I-V Test System (Automated-S211 (T2003B) with built-in software), which has an active area of 0.04 cm^2 . Open-circuit voltage decay (OCVD) was used to study the charge dynamics of the PSCs. Moreover, the photoluminescence spectra of PSC were measured using a photoluminescence spectrometer with a nitrogen laser wavelength of 337.1 nm as an excitation source. Then, the electrochemical impedance spectroscopy was measured by a HIOKI 3522-50 LCR Hi tester.

3. Results and Discussion

3.1. Photovoltaic Performance of Perovskite Solar Cells

Generally, the characteristic parameters of PSCs consist of the short-circuit photocurrent density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor of the cell (FF), and the intensity of incident light (P_{in}). Current density–voltage (J–V) characteristics of fabricated n-i-p heterojunction PSCs of all conditions are measured under standard illumination of 100 mW/cm^2 (AM1.5); this is shown in Figure 2, with the photovoltaic parameters summarized in Table 1. It is found that the PSC devices fabricated with $\text{SnO}_2/\text{SnO}_x$ in ETL exhibit the highest PCE of 18.39% (compared to the device fabricated with TiO_2 compact layer only of 14.57%). The increase in PCE can be described in terms of an increase in J_{sc} and FF . In addition, the $\text{SnO}_2/\text{SnO}_x$ double-layer exhibits the highest PCE due to the fabrication of a p–n junction, which can be explained by the formation of built-in potential and a built-in electric field, resulting in low charge transfer resistance and high charge recombination resistance, as reported in our previous work [27]. In addition, the surface morphology of ETL looks similar, as seen in our previous work and other reported work [27,28], and it has a smaller impact on the device performance, which can be seen from the close value of the current density for all conditions of ETL.

Figure 2. (a) Photovoltaic performance and (b) stability of current density of the perovskite solar cells with the different film multi-layers of ETL.

Table 1. Photovoltaic parameters of PSCs fabricated with the different conditions of ETL.

Device	V_{oc} (V)	J_{sc} (mA/cm²)	FF	PCE (%)	R_{sh} (Ω)	R_s (Ω)
SnO ₂	0.99 (0.97 ± 0.02)	22.70 (21.85 ± 0.93)	73.17 (70.74 ± 2.65)	16.48 (14.95 ± 0.77)	2605.1	3.2
SnO ₂ /SnO _x	1.04 (1.03 ± 0.01)	22.66 (22.08 ± 0.70)	77.94 (76.70 ± 1.93)	18.39 (17.41 ± 0.72)	3035.6	2.8
TiO ₂	0.98 (0.96 ± 0.02)	21.57 (21.13 ± 0.32)	69.08 (65.14 ± 4.50)	14.57 (13.28 ± 1.32)	1345.2	5.6
TiO ₂ /SnO ₂	1.02 (1.00 ± 0.01)	22.23 (22.23 ± 0.44)	73.36 (70.80 ± 2.09)	16.68 (15.82 ± 0.75)	1435.9	3.6
TiO ₂ /SnO ₂ /SnO _x	0.99 (0.99 ± 0.01)	22.74 (22.54 ± 0.21)	77.80 (75.49 ± 1.38)	17.44 (16.84 ± 0.50)	2918.1	3.0

The stability of the fabricated multi-ETL-based PSCs in the current density is shown in Figure 2b. The current density stability of the devices with no encapsulation is measured on a light simulation of 100 mW/cm^2 for 360 s. Normally, T_{80} is defined as the time that the initial current density decays to 80%. It can be seen that the stability of the $\text{SnO}_2/\text{SnO}_x$ double-layer exhibits the highest stability, which is in agreement with the highest efficiency. It should be noted that PSCs with TiO_2 and $\text{TiO}_2/\text{SnO}_2$ exhibit the lowest T_{80} of only about 20 s.

Until recently, the photovoltaic performance of PSCs depended on the number and thickness of ETL. Thus, the photoconversion properties of PSC will be studied in terms of optical and electrical properties, which are studied by photoluminescence spectroscopy (PL), open-circuit voltage decay (OCVD), and electrochemical impedance spectroscopy (EIS), respectively.

3.2. Investigation of Charge Transport of Perovskite Solar Cells

The different multi-ETL conditions of PSCs in photoluminescence spectra are measured by PL for the investigation of photocharge transfer. Figure 3 shows the PL of the perovskite films prepared under different multi-ETL conditions. The $\text{SnO}_2/\text{SnO}_x$ double-layer exhibits the lowest PL intensity caused by the higher photocharge transfer from the perovskite layer to ETL than the other conditions. The higher photocharge transfer of the $\text{SnO}_2/\text{SnO}_x$ double-layer condition can be explained by its lower radiative recombination and lower PL intensity.

Figure 3. Photoluminescence spectra of the perovskite films prepared with the different conditions of ETL (excitation wavelength = 337.1 nm).

To investigate charge recombination, V_{oc} behavior is further studied by OCVD measurements of the PSCs, as shown in Figure 4. V_{oc} decay is shown as a function of time when the light is turned off. The OCVD spectra are fitted and calculated in Table 2. The fitting graph is presented using a biexponential relation

$$V_{oc} = A_1 e^{(-\frac{t}{\tau_1})} + A_2 e^{(-\frac{t}{\tau_2})} \quad (1)$$

where A_1 and A_2 are time-independent coefficients of amplitude fractions for each decay component and τ_1 and τ_2 are the decay times of fast and slow components, respectively. The results are given in Table 2. A_1^* and A_2^* are normalized coefficients obtained from a relation. The longer charge transfer lifetime of PSCs with the multi-ETL rather than the single-ETL can also be seen.

Figure 4. Voc decay of PSCs with the different conditions of ETL as a function of time after turning off the light.

Table 2. OCVD fitted parameters from Equation (1) for PSCs with the different conditions of ETL. A_1^* and A_2^* are normalized coefficients obtained from a relation.

Device	A_1^*	τ_1 (s)	A_2^*	τ_2 (s)	$\tau_{average}$ (s)
SnO ₂	39.14	0.15	60.86	3.49	2.18
SnO ₂ /SnO _x	43.90	0.18	56.10	15.44	8.74
TiO ₂	24.60	0.08	75.40	4.07	3.09
TiO ₂ /SnO ₂	38.50	0.36	61.50	15.70	9.80
TiO ₂ /SnO ₂ /SnO _x	48.91	0.18	51.09	33.64	17.27

For the study of electrical properties, the electron transport, charge recombination, and electron lifetime are characterized by the electrochemical process in EIS. The frequency range used in EIS ranges from 100,000 Hz to 450 Hz, with an AC amplitude under 100 mW/cm² solar light (light condition) and without light (dark condition). The recorded EIS spectra of Nyquist plots of different ETL are shown in Figure 5a,b for light and dark conditions, respectively. The parameters of EIS from the semicircle Nyquist plot are calculated and summarized in Table 3. In Figure 5a, a semicircle (a starting point is at high to low frequency) is observed for all conditions and can be fitted to an equivalent circuit, as seen in the inset. In this range of frequency, R_1 can represent the series resistance, including the contributions from FTO glass and metal electrode, and R_{ct} represents the resistance due to the interface between ETL and the perovskite layer [29,30]. Thus, the effect on the multi-ETL can be investigated by monitoring the value of R_{ct} . In Table 3, the PSCs with the SnO₂/SnO_x conditions exhibit the lowest value of the R_{ct} , resulting in the highest PCE. Moreover, the TiO₂ CP single-layer shows the largest semicircle compared with the other condition, and it exhibits the highest R_{ct} and the lowest PCE. Moreover, the charge recombination resistance (R_{rec}), which can be obtained under the dark conditions in Figure 5b, is related to the recombination sites at the interface of the ETL/perovskite layer, where the higher value represents a smaller chance of carriers being recombined. The PSC with TiO₂/SnO₂/SnO_x under dark conditions demonstrated the largest R_{rec} . The electron

lifetime (τ) can be calculated by Bode phase plots, which are written in terms of angular frequency or frequency as in Equation (2),

$$\tau = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \quad (2)$$

where ω_{max} is the maximum angular frequency and f_{max} is the maximum frequency (the data value can be obtained from the Bode phase plots at the frequency peak in the middle highest spectrum). Figure 6 shows the frequency peak for the PSC of all devices under dark conditions. It was found that the f_{max} of PSCs under the $\text{SnO}_2/\text{SnO}_x$ condition changed to a lower frequency compared with the other conditions. Thus, the higher τ value suggests a longer electron lifetime. From EIS spectra, it should be noted that R_{ct} can be derived from the light condition, but R_{rec} and electron lifetime can be derived from the dark condition.

Figure 5. Nyquist plots of PSCs fabricated with the different conditions of ETL at: (a) light condition and (b) dark condition.

Table 3. Electrochemical parameters fabricated with the different conditions of ETL calculated from EIS analysis.

Device	R_1 (Ω)	R_{ct} (Ω)	R_{rec} (k Ω)	f (Hz)	τ (μ s)
SnO_2	7.5	598	24.6	13000	12.2
$\text{SnO}_2/\text{SnO}_x$	14.5	520	39.1	10000	15.9
TiO_2	8.5	631	16.3	19000	8.4
$\text{TiO}_2/\text{SnO}_2$	10.8	620	31.0	11000	14.5
$\text{TiO}_2/\text{SnO}_2/\text{SnO}_x$	13.6	610	58.2	11000	14.5

Figure 6. Bode phase plots of PSCs fabricated with the different conditions of ETL in dark condition and an equivalent circuit of solar cell in the inset.

3.3. Explanation of Efficiency Enhancement Due to Multi-ETL by EIS

Enhancements in efficiency can be practically explained using R_{ct} and R_{rec} , as earlier discussed. Typically, the lower the R_{ct} , the higher the PCE, and the higher the R_{rec} , the higher the PCE. The lowest R_{ct} is observed in PSC with a $\text{SnO}_2/\text{SnO}_x$ double-layer and the highest R_{rec} is differently observed in a PSC with a triple-layer. However, the PCE is comparable for the $\text{SnO}_2/\text{SnO}_x$ double-layer and triple-layer. The comparable PCE for both cases can be explained using Equation (3) with an equivalent circuit, as shown in an inset of Figure 6:

$$I = I_L - I_D - I_{sh} = I_L - I_0 \exp \left[\frac{q(V + IR_s)}{nkT} \right] - \frac{V + IR_s}{R_{sh}} \quad (3)$$

where I is the cell output current, I_L is the light-generated current, I_D is the dark current, I_{sh} is the shunt current, V is the voltage across the cell terminals, T is the temperature, q and k are constants, n is the ideality factor, R_s is the cell series resistance, and R_{sh} is the cell shunt resistance.

This equation can be divided into three terms. The first term represents the light current or photocurrent and can be related to R_{ct} . The second term represents the dark current and can be related to R_{rec} . The third term represents shunt current and can be related to R_{sh} and R_s .

As such, the PCE of the $\text{SnO}_2/\text{SnO}_x$ double-layer, which has the lowest R_{ct} but lower R_{rec} than that of the triple-layer, exhibits a comparable PCE to the PSC with a triple-layer, as the R_{ct} and R_{rec} parameters create a compensation effect. It can be seen that R_{ct} , which can be derived from the light condition, and R_{rec} , which can be derived from the dark condition, are suitable parameters to explain the efficiency enhancement in PSCs.

Normally, current information in light and dark conditions can be separately observed by PL and OCVD, respectively. However, it can be seen that EIS provides an easy and alternative way to obtain both light and dark conditions in one technique, which is useful information for explaining the enhancement in efficiency that characterizes PSCs.

4. Conclusions

The multi-ETLs in PSCs have been designed and fabricated to investigate the photoconversion performance of EIS. It is found that the PSC devices fabricated with a $\text{SnO}_2/\text{SnO}_x$ double-layer in ETL exhibit the highest PCE of 18.39%. The efficiency enhancement can be discussed in terms of charge transport, charge recombination, and electron lifetime in PSCs. The enhancement in efficiency can be attributed to a decrease in R_{ct} and an increase in R_{rec} . In addition, R_{ct} and R_{rec} can be used to explain the comparable PCE between PSCs with a $\text{SnO}_2/\text{SnO}_x$ double-layer and those with a triple-layer, which is due to the compensation effect of the R_{ct} and R_{rec} parameters. Therefore, R_{ct} , which can be derived from the light condition, and R_{rec} , which can be derived from the dark condition, are appropriate parameters to explain the enhancement in efficiency in PSCs. Thus, R_{ct} and R_{rec} show that the electrochemical impedance spectroscopy technique is an easy and alternative way to obtain information to understand and characterize multi-ETLs in PSCs.

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