

## The effects of electrolyte additives on the cell performances of CdS/CdSe quantum dot sensitized solar cells

Songyi Park, Min-Kyu Son, Soo-Kyoung Kim, Myeong-Soo Jeong, Kandasamy Prabakar, and Hee-Je Kim<sup>\*</sup>

Department Electrical Engineering, Pusan National University, San 30, Jangjeon-dong, Geumjeong-gu, Busan 609-735, Korea  
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**Abstract**—The electrolyte for QDSSCs is normally a polysulfide,  $S^{2-}/S_x^{2-}$ , redox couple. This couple plays an important role for the regeneration of quantum dots. This study examined the effects of the electrolyte for CdS/CdSe QDSSCs. Electrolytes consisting of 1 M  $Na_2S$ , 2 M S in a methanol and water-mixed solution at a 7 : 3 ratio with or without additives such as KCl, NaOH, KOH and NaCl were used for QDSSC. The electrolyte with NaOH showed the highest conversion efficiency, 3.18%. The reasons for the improved photovoltaic characteristics were analyzed using a range of techniques.

**Key words:** Quantum Dot-sensitized Solar Cells, CdS, CdSe, Polysulfide Electrolyte, Electrolyte Additives

### INTRODUCTION

Quantum dot-sensitized solar cells (QDSSCs) are considered an alternative to dye-sensitized solar cells (DSSCs) which have been studied extensively over the past two decades owing to the special characteristics of quantum dots [1-7]. One of the best advantages of QDSSCs is multiple exciton generation, which can improve the conversion efficiency by creating additional electron-hole pairs using excess energy [8]. Other merits include the simply tunable band-gap by changing the quantum-dot size and high extinction coefficient [9,10].

Semiconductor quantum dots, such as CdS, CdSe, PbS and PbSe, have been used as alternatives to the dye [11-14]. Among these quantum dot materials, CdS and CdSe have attracted considerable attention because of their suitable band gap for efficient charge transfer to  $TiO_2$  [15]. On the other hand, CdS, as a sensitizer for QDSSCs, has light absorption limits owing to its large bandgap. Therefore, CdSe which has a relatively small bandgap also needs to more absorb a wider wavelength of light [16].

The working principle of QDSSCs is similar to that of DSSCs. First, the sensitizers, quantum dots, absorb light and undergo photo-excitation. The electrons are injected into the conduction band of  $TiO_2$ . The quantum dots are regenerated by the redox system, which itself is regenerated at the counter electrode by the electrons passing through the load [17-20]. The electrolyte plays an important role in sensitizer regeneration among this mechanism of QDSSCs. This means that the electrolyte properties affect the performance of QDSSCs. The polysulfide  $S^{2-}/S_x^{2-}$  was reported to be a suitable redox couple for stabilizing the quantum dots compared to the others [21-23].

In this study, the electrolyte components were changed, but  $Na_2S$ , S and solvent were the same. The electrolyte elements without additive contained concentrations of 1 M  $Na_2S$ , 2 M S and methanol : water 7 : 3 (v : v), as referred to literature [24]. The role of the  $Na_2S$  is the source of  $S^{2-}$  ions, which is needed for hole recovery, S is a

source of  $S_x^{2-}$  ions that helps improve hole recovery, and KOH is used to enhance the conductivity and mixed solvent overcomes the high surface tension of water, which makes electrolyte penetration difficult, and improves the good dissociation ability of water [25]. NaOH, KOH and NaCl were used to enhance the electrolyte performance instead of KCl that is commonly used. The electrolyte contains only  $Na_2S$ , and S was also studied for comparison. Other additives were evaluated to determine if there were other effects on the QDSSCs performance. The QDSSCs with these five types of electrolyte characteristics were analyzed.

### EXPERIMENTAL PROCEDURES

#### 1. Fabrication of QDSSCs

Cleaned commercial FTO glass (12  $\Omega$ /sq., Hartford Glass Co. Inc.) was used as electrode substrates. An approximately 8  $\mu$ m thick  $TiO_2$  nanocrystalline (Ti-Nanoxide HT/SP, Solaronix) layer with a 0.25  $cm^2$  active area was deposited using the doctor blade method. The layer thickness was confirmed by cross sectional scanning electron microscopy (SEM, S-4800, Hitachi Co.). All chemicals used to fabricate the sensitizers were purchased from Sigma-Aldrich and used without further purification. For deposition of quantum dots, we used successive ionic layer absorption and reaction (SILAR) method for CdS and chemical bath deposition (CBD) for CdSe. CdS quantum dots were coated on the  $TiO_2$  layer by immersing in the Cd source solution and S source solution by turns at room temperature. The  $TiO_2$  layer was immersed in a 0.2 M  $Cd(CH_3COO)_2$  aqueous solution for 5 minutes, and washed with water and ethanol. Subsequently, the  $TiO_2$  layers were immersed in a 0.2 M  $Na_2S$  aqueous solution for 5 minutes, and washed with water and ethanol. These processes comprised a single cycle. Three cycles were performed to deposit CdS quantum dots on  $TiO_2$ . CdSe was attached to  $TiO_2$ /CdS by CBD method. The photoelectrode was immersed into a CdSe aqueous solution containing 0.01 M  $Na_2SeSO_3$ , 0.0025 M  $Cd(CH_3COO)_2$  and 0.075 M  $NH_4OH$  at 90 °C for 30 minutes. The photoanode was then washed with water and dried. The CuS counter electrode was deposited on two holes drilled into the FTO glass using the CBD method. The counter electrode substrate was dipped into

<sup>\*</sup>To whom correspondence should be addressed.  
E-mail: heeje@pusan.ac.kr

an aqueous CuS solution containing 0.1 M CuSO<sub>4</sub>, 1 M thioacetamide and 0.7 M acetic acid at 90 °C for 30 minutes. The prepared photo-electrode and counter electrode were sealed with a 50 µm hot melt sealing sheet (SX 1170050, Solaronix). Finally, five different types of electrolytes consisting of 1 M Na<sub>2</sub>S and 2 M S in 7 : 3 methanol : water (v : v) with no (Electrolyte 1) or 0.2 M KCl (Electrolyte 2) or 0.2 M NaOH (Electrolyte 3) or 0.2 M KOH (Electrolyte 4) or NaCl (Electrolyte 5) were filled through the drilled holes.

## 2. Measurements

The surface morphology of the TiO<sub>2</sub> layers absorbed CdS and CdSe was examined by SEM with a 15 kV accelerating voltage. The elemental composition of the photoanodes was analyzed by energy dispersive X-ray spectroscopy (EDS) attached to the SEM equipment under the same condition. The photovoltaic performance was measured under 1 sun (100 mW/cm<sup>2</sup>) or in the dark using a solar simulator (Model 2400, Keithley Instrument, Inc.). The internal resistance was confirmed by electrochemical impedance spectroscopy (EIS, SP-150, Biologic SAS) over the frequency range, 10 mHz to 500 kHz. Open circuit voltage decay was measured using a solar simulator (Model 2400, Keithley instrument, Inc.) by switching off the light from steady illumination of 1 sun.

## RESULTS AND DISCUSSION

Fig. 1 shows these three surface SEM images and the pictures of these photoelectrodes. Fig. 1(a) presents the TiO<sub>2</sub>, CdS-deposited TiO<sub>2</sub> (TiO<sub>2</sub>/CdS) and CdS and CdSe deposited TiO<sub>2</sub> (TiO<sub>2</sub>/CdS/CdSe) electrodes. The surfaces of the TiO<sub>2</sub>/CdS and TiO<sub>2</sub>/CdS/CdSe

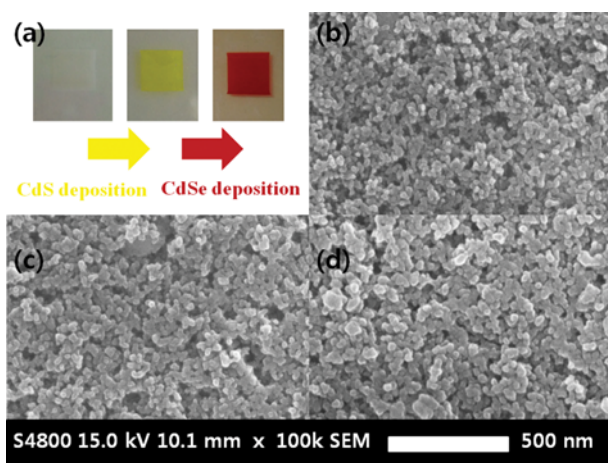


Fig. 1. (a) Photographs of TiO<sub>2</sub>, TiO<sub>2</sub>/CdS and TiO<sub>2</sub>/CdS/CdSe photoanode, FE-SEM images of (b) the bare TiO<sub>2</sub>, (c) TiO<sub>2</sub>/CdS and (d) TiO<sub>2</sub>/CdS/CdSe.

changed to yellow and dark red colors after deposition of QDs compared with those of TiO<sub>2</sub>. The morphology of the TiO<sub>2</sub> (Fig. 1(b)), TiO<sub>2</sub>/CdS (Fig. 1(c)) and TiO<sub>2</sub>/CdS/CdSe (Fig. 1(d)) surfaces was examined by SEM. The surface morphology was similar regardless of whether the TiO<sub>2</sub> had been sensitized, because the size of CdS and CdSe quantum dots was too small to be observed by SEM. On the other hand, the overall size of the particles of TiO<sub>2</sub> increased slightly. These sensitizers deposited on TiO<sub>2</sub> were predicted to have a core shell structure. EDS results also revealed the formation of CdS and CdSe in Table 1. The atomic percentage of Ti and O decreased from 32.7% and 67.3% to 26.2% and 66.6%, respectively, with the concomitant appearance of cadmium (3.2%) and sulfur (4%) after the deposition of CdS on TiO<sub>2</sub>. These percentages decreased further to 22.7% and 63.2% with further increases in the atomic percentage of cadmium to 8%. At the same time, the percentage of sulfur decreased slightly to 2.5% and the atomic percent of selenium was 3.5%, confirming the formation of CdSe on TiO<sub>2</sub>/CdS.

Table 2 lists the photovoltaic properties of QDSSCs using five kinds of electrolyte,  $V_{oc}$ ,  $J_{sc}$ , FF and efficiency, and Fig. 2 shows these photovoltaic properties' average value with error bars. The efficiency can be obtained using these values from this equation:

$$\text{Efficiency (\%)} = \frac{V_{oc} \times J_{sc} \times FF}{100 \text{ (mWcm}^{-2}\text{/cm}^2\text{)}}$$

The QDSSC using electrolyte1 indicated lowest photovoltaic performances as compared with others. The existence of additives definitely improved the photovoltaic properties. These four types of additives enhanced these properties differently: improving the open circuit voltage ( $V_{oc}$ ) or short circuit current ( $J_{sc}$ ) or fill factor (FF). The QDSSCs with Electrolyte 2 containing KCl, which is normally used as an additive for QDSSCs electrolyte, showed highest  $J_{sc}$ . The high conductivity led to high  $J_{sc}$  but voltage and FF were relatively low. The QDSSC using Electrolyte 3, which consisted of 1 M Na<sub>2</sub>S, 2 M S and 0.2 M NaOH in methanol : water 7 : 3 (v : v)

Table 1. Atomic percent of Ti, O, Cd, S and Se on the surface of the TiO<sub>2</sub>, TiO<sub>2</sub>/CdS and TiO<sub>2</sub>/CdS/CdSe measured by EDS with a 15 kV accelerating voltage

Element	TiO <sub>2</sub>	TiO <sub>2</sub> /CdS	TiO <sub>2</sub> /CdS/CdSe
Atomic percent of Ti (%)	32.7	26.2	22.7
Atomic percent of O (%)	67.3	66.6	63.2
Atomic percent of Cd (%)	0	3.2	8
Atomic percent of S (%)	0	4	2.5
Atomic percent of Se (%)	0	0	3.5

Table 2. Open circuit voltage ( $V_{oc}$ ), short circuit currents densities ( $J_{sc}$ ), fill factor (FF) and conversion efficiency ( $\eta$ ) of QDSSCs using different electrolyte (Electrolyte 1 to 5)

Cell	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	Efficiency (%)
Electrolyte 1	0.56±0.004	10.88±0.338	0.45±0.007	2.79±0.070
Electrolyte 2	0.57±0.008	11.76±0.359	0.46±0.002	3.06±0.083
Electrolyte 3	0.59±0.003	11.00±0.351	0.49±0.011	3.18±0.027
Electrolyte 4	0.57±0.004	10.56±0.142	0.51±0.008	3.05±0.024
Electrolyte 5	0.57±0.003	11.00±0.110	0.47±0.004	2.95±0.042

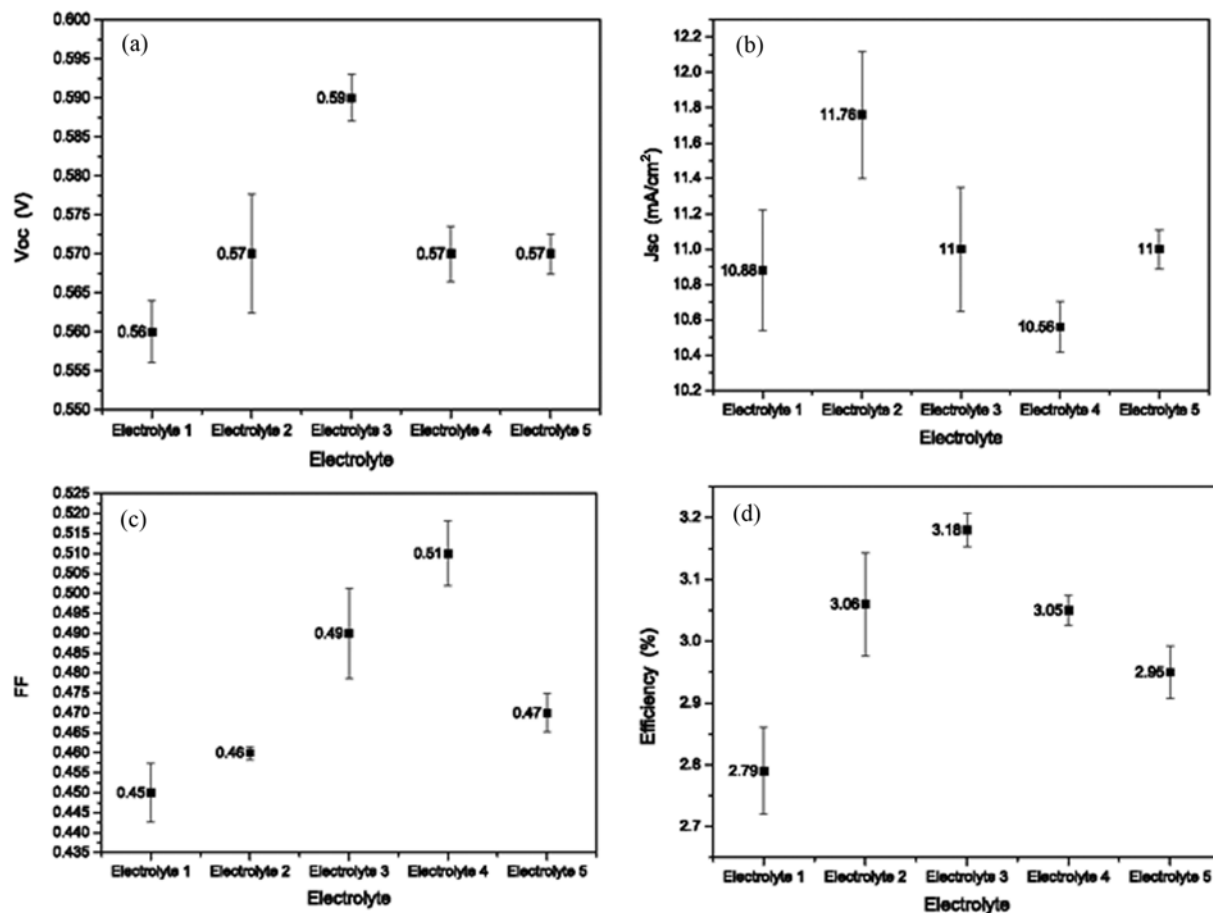


Fig. 2. Photovoltaic properties, (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c) FF and (d) efficiency, of QDSSCs using various electrolytes (Electrolyte 1 to 5) measured under the 1 sun ( $100 \text{ mW}/\text{cm}^2$ ).

solution, showed the highest conversion efficiency, 3.18%, with a relatively higher  $V_{oc}$  and FF. The reasons for improved photovoltaic properties are discussed with the results of EIS, dark current and open circuit voltage decay. EIS results with equivalent circuit in Fig. 3 were used to study the kinetics of electrochemical and photoelectrochemical processes occurring in QDSSCs [26,27].  $R_s$  which is resistance in the high-frequency range over 500 kHz, is related to ohmic

serial resistances.  $R_{ct1}$  is counter electrode/electrolyte interface resistance,  $R_{ct2}$  is  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{electrolyte}$  interface resistance, and  $Z_w$  which is overlapped by  $R_{ct2}$  is ion diffusion within the electrolyte impedance. The overall charge transport resistances, the sum of  $R_s$ ,  $R_{ct1}$ ,  $R_{ct2}$  and  $R_w$ , of QDSSCs with Electrolyte 4, Electrolyte 3 and Electrolyte 2 were smaller than those of QDSSC with Elec-

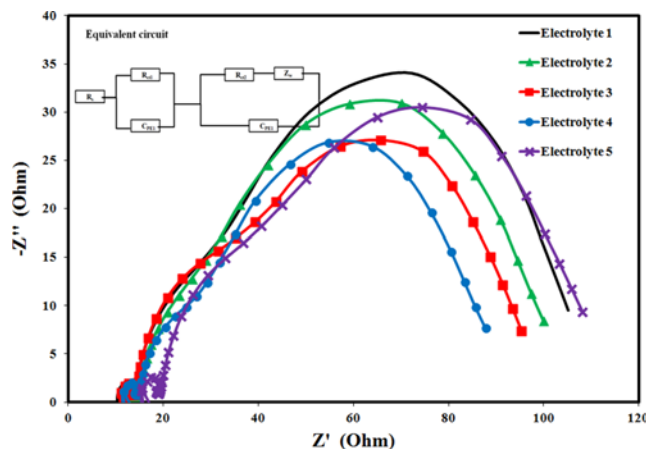


Fig. 3. EIS spectra of QDSSCs using various electrolytes (Electrolyte 1 to 5) measured under the 1 sun ( $100 \text{ mW}/\text{cm}^2$ ).

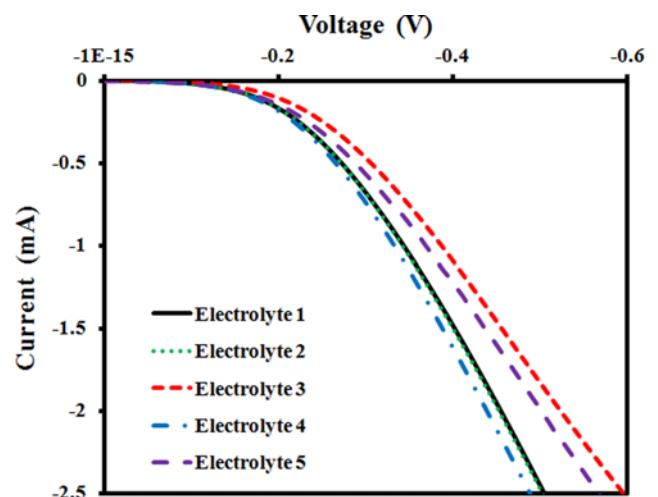


Fig. 4. Dark current of QDSSCs using various electrolytes (Electrolyte 1 to 5) measured in the dark.

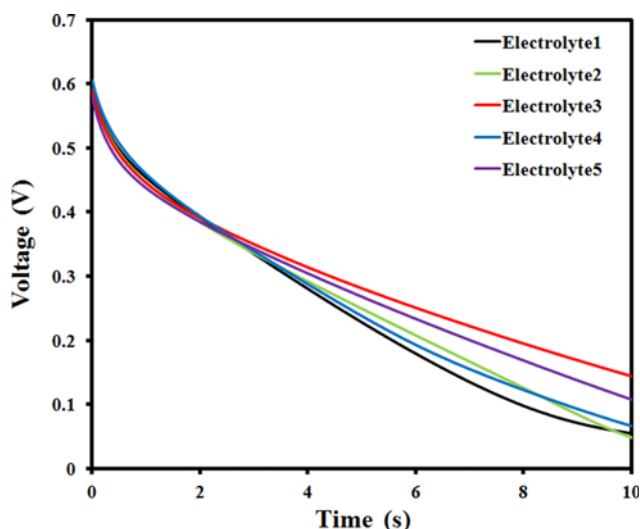


Fig. 5. The open circuit voltage decay of QDSSCs using various electrolytes (Electrolyte 1 to 5) with time.

trollyte 1. This indicated that additives were improving electrolyte diffusion leading to enhancement of charge transport in the QDSSCs. FF of QDSSC is related to charge transport of electrons at photoanode/electrolyte [28]. In other words, QDSSCs using polysulfide electrolyte with additives improved charge transport of electrons indicating higher FF. Fig. 4 presents the dark current corresponding to the recombination of electrons with the electrolyte. The steeper slope means the more recombination occurs in the QDSSCs resulting in lower  $V_{oc}$  [29,30]. From comparing the slopes of dark current graph, the QDSSC with Electrolyte 3 had lower slopes relatively, and this affected on higher  $V_{oc}$ . For further verification of recombination mechanism, open circuit voltage was measured in Fig. 5. The QDSSCs were illuminated to a steady state 1 sun and then open circuit voltages were measured after abrupt switching off of the light. The voltage decay with time is inversely proportional to electron life time according to life time equation [31].

$$\tau = -\frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

Where  $k_B$  is the Boltzmann constant ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ ),  $T$  is the absolute temperature (298 K), and  $e$  is the electronic charge ( $1.602 \times 10^{-19} \text{ C}$ ). The rapid decrease of open circuit voltage with time means short life time of electron caused by more recombination of electrons occurring in the QDSSCs. Therefore, the electron recombination in the QDSSCs with Electrolyte 3 whose open circuit voltage showed the slowest decrease was least among QDSSCs with other electrolytes. And these results correspond with dark current.

## CONCLUSION

This study examined the effects of difference electrolytes with or without various additives for CdS/CdSe QDSSCs. SEM and EDS revealed the formation of CdS and CdSe. The influences according to the additives to the electrolyte were not remarkable. On the other hand, the existence of additives definitely improved the photovoltaic properties. The QDSSC using Electrolyte 3, which consisted of 1 M  $\text{Na}_2\text{S}$ , 2 M S and 0.2 M NaOH in a methanol : water 7 : 3

(v : v) solution, showed the highest conversion efficiency, 3.18%. QDSSCs using Electrolyte 3 indicated a relatively higher FF due to the relatively small overall internal resistance, meaning high charge transport of electrons and highest  $V_{oc}$  due to lower recombination confirmed by dark current and open circuit voltage decay.

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