A New Polymer Electrolyte for Solid-State Quantum Dot Sensitized Solar Cells

Ying Yang and Wenyong Wang*

Department of Physics & Astronomy, University of Wyoming, Laramie, WY 82071, USA

Abstract: Liquid electrolytes in quantum dot sensitized solar cells (QDSSCs) cause device packaging and stability issues, and in this work a new type of solid-state electrolyte based on PEO-PVDF polymer blends with S/tetramethylammonium sulfate (S/TMAS) redox additive is investigated. UV-Vis and ionic conductivity measurements are performed to characterize the electrolytes' optical and electrochemical properties. QDSSCs are fabricated using the polymer electrolytes, and a possible additional redox process in the cells is proposed. The study shows that the PEO-PVDF polymer electrolyte with the S/TMAS redox additive can improve the solar cell incident photon-to-current conversion efficiency and stability. This research could shed light on the study of novel solid-state QDSSCs based on polymer electrolytes with further enhanced performance.

Keywords: Polymer Electrolyte, Redox Couple, Solar Cells, Stability

* Corresponding author. Tel.: +1 (307) 766-6523; Fax: +1 (307) 766-2652; E-mail: wwang5@uwyo.edu.

1. Introduction

It is well known that liquid electrolytes in quantum dot sensitized solar cells (QDSSCs) have issues such as being volatile and corrosive, which cause difficulties in device packaging and decrease the long-term stability of the cells [1]. On the other hand, solid-state electrolytes have been widely studied in the past, and most of the research has been carried out on dye sensitized solar cells (DSSCs) [2]. Research on all solid-state quantum dot sensitized solar cells has attracted more attention recently, and it is expected that the application of solid-state or quasi solid-state electrolytes in QDSSCs could substantially improve their performance by reducing QD corrosion and device degradation as well as realizing a faster hole regeneration [3]. Typical all solid-state QDSSCs are based on mesoporous TiO_2 nanoparticle films, CdSe or PbS QD sensitizers, and solid-state hole conductors such as spiro-OMeTAD [1]. However, one major issue with most solid-state hole transporting materials is the poor penetration into mesoporous photoanode thin films, which limits film thickness and lowers the light harvesting efficiency. In this study we investigate polymer-based solid-state electrolytes for QDSSCs, which have the advantages of easy penetration into porous films, good wettability with the nanostructured photoanodes, and relatively high ionic conductivity [4]. Polymer electrolytes have been inspected for different applications in the past, such as in Lithium ion batteries or DSSCs [5]. However, to the best of our knowledge, thus far there are only limited reports on their applications in QDSSCs [6].

Typical liquid electrolytes used for QDSSCs are aqueous polysulfide solutions with the $\text{S}^{2-}/\text{S}_x^{2-}$ redox couple [7-9], and this redox couple plays a key role in the regeneration of the

semiconductor QDs by scavenging the photogenerated holes [10]. In such liquid electrolytes, the oxidization at the photoanode/electrolyte interface can be described as [11,12]:

S_x^{2-} is then reduced to S^{2-} at the counter electrode in the regeneration process [13]:

Popular redox additives used to generate the S^{2-}/S_x^{2-} redox couple in liquid electrolytes include S/Na₂S in water [14], Na₂S in alkaline aqueous solution [15], and recently reported [(CH₃)₄N]₂S/S in organic solvent [16]. However, for polymer-based solid-state electrolytes thus far there are only limited studies of new types of redox additives [17]. In this work, we utilize S/tetramethylammonium sulfate (S/TMAS) as the redox additive to create polymer electrolytes based on Poly(ethylene oxide)-Poly(vinylidene fluoride) (PEO-PVDF). Their properties are characterized and are compared with those of the polymer electrolytes with the S/Na₂S redox additive. QDSSCs are also fabricated using these polymer electrolytes, and the incident photon-to-current conversion efficiency (IPCE) measurement results show that the new type of polymer electrolyte with the S/TMAS redox additive can improve the solar cell IPCE and enhance their stability.

2. Experimental methods

2.1 Sample preparation

Poly(ethylene oxide) (PEO, $M_w = 4 \times 10^5$ g/mol, Sigma-Aldrich, St. Louis, MO, USA),

63 Poly(vinylidene fluoride) (PVDF, Sigma-Aldrich), tetramethylammonium sulfate (TMAS,
64 $[(\text{CH}_3)_4\text{N}]_2\text{SO}_4$, 99%, Fluka, Sigma-Aldrich, St. Louis, MO, USA), sulfur powder (S, 99.5%,
65 Alfa Aesar, Ward Hill, MA, USA), propylene carbonate (PC, Sigma-Aldrich),
66 1,2-dimethoxyethane (DME, Sigma-Aldrich), TiO_2 (P25, 20 - 30 nm, Acros Organics,
67 Thermo Fisher, Waltham, MA, USA), zinc nitrate hydrate $(\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O})$, 99%, Alfa Aesar),
68 sodium sulfide nonahydrate $(\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O})$, 98%, Sigma-Aldrich), cadmium nitrate tetrahydrate
69 $(\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O})$, 98%, Sigma-Aldrich), selenium dioxide (SeO_2 , 99.9%, Sigma-Aldrich),
70 and sodium borohydride (NaBH_4 , 99%, Fluka) were used in this study.

71 The TiO_2 photoanode film was prepared by the doctor-blade technique. TiO_2 (P25) paste
72 was deposited on a conducting glass substrate (F-doped SnO_2 , 10 Ω/square , MTI, Richmond,
73 CA), and was sintered at 450 $^\circ\text{C}$ for 30 min. The thickness of the film was 10 μm .

74 CdSe/ZnS quantum dot layer was deposited on the TiO_2 photoanode by the successive ionic
75 layer adsorption and reaction (SILAR) method. 30 mM $\text{Cd}(\text{NO}_3)_2$ in ethanol, 100 mM $\text{Zn}(\text{Ac})_2$
76 in water, and 100 mM $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in water were prepared separately and were stored in a
77 glove box. To prepare the selenide ion precursor solution (Na_2Se , 30 mM) for CdSe deposition,
78 0.16643 g of SeO_2 was dissolved first in 50 mL ethanol under stirring, and 0.11348 g of
79 NaBH_4 (60 mM) was added into the above solution and stirred for 1 hour inside a glove box.
80 Each SILAR coating cycle consisted of successive immersion of the TiO_2 electrode in the Cd^{2+}
81 and Se^{2-} ion solutions for 1 min each, and the SILAR cycle was repeated for 5 times. For ZnS
82 deposition, the CdSe-coated TiO_2 electrode was successively immersed in the Zn^{2+} and S^{2-} ion
83 solutions for 1 min each, and this coating was repeated for 2 times. All SILAR coating was
84 carried out in a glove box filled with Ar.

To prepare the PEO-PVDF polymer electrolytes, 0.16 g PEO and 0.24 g PVDF were dissolved in 15 g of DME/PC (3:7, v/v) co-solvent under continuous stirring at 80 °C for 4 h in a water bath. Solid S and TMAH with different S/TMAH molar ratios (0.3, 0.7, 1.3, 2, 3, 4, 5, 7, 11, and 14) were then added at room temperature, during which the total mass of S and TMAH was kept at 0.0488 g. The electrolyte solution was then stirred for 5 days to form a homogeneous viscous liquid. PEO-PVDF polymer electrolytes with pure S, pure TMAH, or S/Na₂S (S/Na₂S molar ratio of 3 with a total mass of 0.0488 g) were also prepared for comparison studies, and the preparation procedure is similar.

To fabricate solid-state QDSSCs, the polymer electrolyte solution was applied on the CdSe/ZnS-coated TiO₂ photoanode, and the substrate was put into an oven at 80 °C. When the electrolyte became viscous, a platinum plate counter-electrode was put on the surface of the electrolyte/photoanode assembly. The device was further stored in the oven at 80 °C for another 2 h to completely remove the solvent in the electrolyte, and a sandwich-typed solid-state QDSSC was created.

2.2 Sample characterization

The morphology of the PEO-PVDF polymer electrolyte films with the S/TMAH or S/Na₂S redox additives was analyzed by a Quanta 450 FEG Field Emission Scanning Electron Microscope (FEI, Hillsboro, Oregon, USA). UV-Vis absorption spectra of the PEO-PVDF polymer electrolytes were obtained using a Lambda 950 UV-Vis Spectrometer (PerkinElmer, Waltham, MA, USA). ATR-FTIR measurements of the polymer electrolytes were performed using a GladiATR Spectrum Two FTIR Spectrometer (PerkinElmer) from 4000 to 400 cm⁻¹

using the transmission mode. The ionic conductivity of the polymer electrolyte was measured using a Compact Stat.e10800 Electrochemical Analyzer (Ivium) from 1 Hz to 1 MHz with a signal amplitude of 10 mV. IPCE was measured under 100 W Quartz Tungsten lamp with an Oriel 1/8 m Comerstone Monochromator (Newport Corporation, Irvine, CA, USA) from 340 - 800 nm, and the lock-in technique was used to acquire the photocurrent at short-circuit condition. **Stability tests of the QDSSCs were carried out at different aging times without device sealing. The IPCE measurements were conducted under ambient conditions, and after each measurement the samples were kept in a dark storage unit at room temperature.**

3. Results and discussion

3.1 Morphology of PEO-PVDF electrolytes with S/TMAS and S/Na₂S additives

Fig. 1a and b show scanning electron microscopy images of PEO-PVDF electrolyte membranes with the S/TMAS and S/Na₂S redox additives, respectively, and in both electrolytes the sulfur concentration is 0.02 M (the molar ratio of S/TMAS or S/Na₂S is 3). It can be seen from Fig. 1 that the electrolyte film with the S/TMAS redox additive exhibits a smooth and continuous surface morphology, while the electrolyte film with the S/Na₂S additive displays a surface with rough aggregates and pores.

3.2 UV-Vis absorption study of PEO-PVDF polymer electrolytes with different redox additives and S/TMAS molar ratios

Fig. 2a shows the UV-Vis absorption spectra of the PEO-PVDF polymer electrolytes with S,

S/TMAS [M(S) = 0.02 M, S/TMAS molar ratio = 3], and S/Na₂S [M(S) = 0.02 M, S/Na₂S molar ratio = 3] additives. The electrolytes exhibit absorption bands around 218 and 264 nm, which correspond to the absorption of thiosulfate S₂O₃²⁻ and polysulfide S_x²⁻, respectively [18,19]. In the PEO-PVDF electrolyte with S/Na₂S, the formation of S_x²⁻ is attributed to the following reactions [18]:

In the electrolyte with S but without Na₂S, S_x²⁻ can be formed differently according to previously published studies related to the hydrolysis reaction of zero-valent sulfur and sulfide oxidation in weakly acidic solutions [20-22]:

In the PEO-PVDF electrolyte with S/TMAS, S_x²⁻ can also be formed from the S content as described in eq. (6) - (8). In Fig. 2a, the PEO-PVDF polymer electrolytes with S or S/TMAS exhibit obvious absorption band of thiosulfate S₂O₃²⁻ at ~ 218 nm, and the electrolyte with S/Na₂S also shows a weak absorption peak at this wavelength. The formation of S₂O₃²⁻ in the electrolytes is due to the fact that polysulfide is highly reactive and undergoes rapid oxidation reaction with oxygen [22]:

The preparation of the PEO-PVDF electrolytes in air and a water bath (80 °C) makes it easy for water and oxygen to react with S, and the reactions proceed as discussed above, which

produce $S_2O_3^{2-}$ and S_x^{2-} in the electrolytes. From Fig. 2a it also can be seen that the addition of TMAS in the electrolyte increases the absorption intensity of $S_2O_3^{2-}$. In organic synthesis, quaternary ammonium salts are typically utilized as phase transfer catalysts, which can accelerate the reactions between reagents dissolved in immiscible solvents [23]. Therefore, the effect of TMAS on $S_2O_3^{2-}$ absorption intensity indicates that it plays the role of a catalyst in the electrolyte to promote the formation of $S_2O_3^{2-}$.

Fig. 2b shows the UV-Vis absorption spectra of the PEO-PVDF polymer electrolytes with different S/TMAS molar ratios, and the inset shows the influence of the S/TMAS molar ratio on the absorption intensity at 218 and 264 nm that are associated with $S_2O_3^{2-}$ and S_x^{2-} , respectively. It can be seen that increasing the S/TMAS molar ratio in the electrolytes leads to increased absorption of $S_2O_3^{2-}$ and S_x^{2-} . The enhanced absorption of S_x^{2-} can be attributed to the increased S concentration in the electrolytes when the S/TMAS molar ratio becomes larger, which promotes the reactions described in eq. (6) - (8). According to eq. (9), this increase in S_x^{2-} concentration further causes an increase in $S_2O_3^{2-}$ concentration, and hence an increase in the absorption intensity of $S_2O_3^{2-}$ as shown in Fig. 2b [21].

3.3 Solid-State QDSSCs based on PEO-PVDF polymer electrolytes with S/TMAS and S/Na₂S redox additives

It has been confirmed that the sulfide ion S^{2-} is only formed in strong alkaline Na₂S solution (e.g., $M(OH^-) = 18 M$), and the UV-Vis absorption band of S^{2-} is around 250 nm [24]. In most electrolytes with S/Na₂S in aqueous solution or in organic solvent that contains water, the sulfide ion S^{2-} exists predominantly as HS^- and the frequently referred S^{2-}/S_x^{2-} redox couple is

in fact $\text{HS}^-/\text{S}_x^{2-}$ [25]. For the PEO-PVDF polymer electrolytes with the S/TMAS or S/ Na_2S additives studied in this work, the absorption bands of either HS^- at ~ 230 nm or S^{2-} at ~ 250 nm are not observed in the UV-Vis spectra shown in Fig. 2, indicating that their concentrations in the electrolytes are insignificant [18]. Based on this observation, in addition to the redox circle that is described by eq. (1) - (3), there could be another possible redox circle in the QDSSCs prepared with the PEO-PVDF polymer electrolytes with S/TMAS or S/ Na_2S redox additives. This additional redox process is illustrated in Schematic 1. In the PEO-PVDF electrolyte with S/TMAS, S works as the source to form S_x^{2-} as suggested in eq. (6) - (8), and TMAS acts as the catalyst to promote the formation of S_x^{2-} . While in the PEO-PVDF electrolyte with S/ Na_2S , both S and Na_2S can serve as the source to form S_x^{2-} by hydrolysis reactions as suggested in eq. (4) - (8). In the PEO-PVDF electrolyte with either S/TMAS or S/ Na_2S , $\text{S}_2\text{O}_3^{2-}$ can be formed by oxidation of the polysulfide ions in the electrolyte as described by eq. (9) [21]. $\text{S}_2\text{O}_3^{2-}$ can act as an oxidizing agent that traps electrons at the electrolyte/counter electrode interface and produces S^{2-} in the electrolyte as shown in Schematic 1 [26]. Meanwhile, the excess polysulfide ions S_x^{2-} can also serve as the electron scavenger at the electrolyte/counter electrode interface. While at the TiO_2 /electrolyte interface the holes are removed by S^{2-} , and the whole redox process in the PEO-PVDF polymer electrolytes can then be described by [18,20-22,26]:

3.4 Ionic conductivity of PEO-PVDF electrolytes with different redox additives and S/TMAS molar ratios

Fig. 3a shows the ionic conductivity of the PEO-PVDF polymer electrolytes with different redox additives of S/TMAS [$\text{M}(\text{S}) = 0.02 \text{ M}$, S/TMAS molar ratio = 3] and S/ Na_2S [$\text{M}(\text{S}) = 0.02 \text{ M}$, S/ Na_2S molar ratio = 3]. It can be seen that the ionic conductivity of the electrolyte with S/TMAS is significantly higher than that of the electrolyte with S/ Na_2S . This increased ionic conductivity can be attributed to the smoother and more continuous surface morphology of the S/TMAS modified PEO-PVDF electrolyte as shown in Fig. 1, which is expected to form efficient ion transport channels in the electrolyte and results in a faster ion transport [27]. In addition, the higher anion concentration in the PEO-PVDF-S/TMAS electrolyte, as suggested by Fig. 2a, can also contribute to this conductivity improvement [28].

Fig. 3b shows the dependence of the ionic conductivity of the PEO-PVDF-S/TMAS electrolytes on S/TMAS molar ratio. The ionic conductivity of the electrolyte with an S/TMAS molar ratio of 0.3 is $0.13 \text{ mS}\cdot\text{cm}^{-1}$. When the S/TMAS molar ratio is increased, an improvement in the ionic conductivity is observed, with the maximum value of $0.63 \text{ mS}\cdot\text{cm}^{-1}$ obtained for the electrolyte with an S/TMAS molar ratio of 3. However, further increasing the molar ratio beyond 3 causes a decrease in the ionic conductivity of the electrolytes.

ATR-FTIR measurements were carried out in order to better understand the interactions between different components in the synthesized polymer electrolytes as well as the ionic conductivity change. Fig. 4 shows the ATR-FTIR spectra of PEO-PVDF, PEO-PVDF-S, PEO-PVDF-TMAS, PEO-PVDF-S/ Na_2S (S/ Na_2S molar ratio = 3), and PEO-PVDF-S/TMAS

with different S/TMAS molar ratios. Fig. 4a, 4b, and 4c exhibit these ATR-FTIR spectra in the wavelength range of 4000 - 400 cm^{-1} , 1050 - 910 cm^{-1} , and 650 - 550 cm^{-1} , respectively.

The absorption bands at 3300 - 3500, 2885, 1404, and 1100 cm^{-1} in Fig. 4a are assigned to the vibration modes of $\nu(\text{OH})$, $\nu(\text{CH})$, $\nu(\text{CF})$, and $\nu(\text{COC})$ in the PEO-PVDF polymer matrix, respectively [29]. The asymmetric stretching mode of $\nu(\text{C}_4\text{N})$ from the TMAS molecules also appears at $\sim 948 \text{ cm}^{-1}$ in the spectrum of the PEO-PVDF-TMAS polymer film [30]. However, it can be seen from Fig. 4b and 4c that new absorption bands are formed at wavelengths of 1023 and 614 cm^{-1} , which only show up in the spectra of the PEO-PVDF-S/TMAS and PEO-PVDF-S/ Na_2S polymer electrolytes. As discussed above, thiosulfate anion $\text{S}_2\text{O}_3^{2-}$ is formed in the PEO-PVDF polymer electrolytes with S/TMAS or S/ Na_2S redox additives. This anion is subjected to cross-linking with cations, and the $[(\text{CH}_3)_4\text{N}]^+$ ion in TMAS and the Na^+ ion in Na_2S may interact with $\text{S}_2\text{O}_3^{2-}$ and form amine-sulfate intermediate complexes such as $[(\text{CH}_3)_4\text{N}]^+ \cdots \text{S}-\text{SO}_3^{2-}$ and $\text{Na}^+ \cdots \text{S}-\text{SO}_3^{2-}$ in the PEO-PVDF-S/TMAS and PEO-PVDF-S/ Na_2S electrolytes, respectively [31,32]. Based on previously studies, the new absorption bands at 1023 and 614 cm^{-1} can be associated with the absorption of $\nu(\text{SO}_3)$ in the intermediate complexes [32]. As can be seen from Fig. 4b and 4c, when the S/TMAS molar ratio is increased, the absorption intensities of $\nu(\text{SO}_3)$ at 1023 and 614 cm^{-1} also increase, indicating an increased number of newly formed amine-sulfate intermediate complexes. This increase in the amine-sulfur intermediate complexes can reduce the amount of free, moveable cations/anions in the electrolyte, which can decrease the ionic conductivity. Therefore, in Fig. 3b the increase in the ionic conductivity with increased S/TMAS molar ratio in the range of 0.3 - 3 can be associated with the increased anion concentration as discussed previously.

However, when the S/TMAS molar ratio is further increased, the increased formation of intermediate complexes surpasses the anion concentration increase and leads to decreased ionic conductivity. In addition, when the S/TMAS molar ratio becomes larger, sulfur aggregation is expected to happen due to limited sulfur solubility in the organic solvent and the viscosity of the polymer electrolyte is expected to rise, which can be another factor that causes the ionic conductivity decrease.

On the other hand, it can be seen from the absorption spectra of the PEO-PVDF-S/Na₂S and PEO-PVDF-S/TMAS (S/TMAS molar ratio = 3) electrolytes, especially from Fig. 4c, that the peak intensity of Na⁺⋯S-SO₃²⁻ is higher than that of [(CH₃)₄N]⁺⋯S-SO₃²⁻, suggesting a higher number of intermediate complexes in the PEO-PVDF-S/Na₂S electrolyte than that in the PEO-PVDF-S/TMAS (S/TMAS molar ratio = 3) electrolyte. In addition to the previously discussed surface morphology and anion concentration effects, this may also contribute to the lower ionic conductivity of the PEO-PVDF-S/Na₂S electrolyte.

3.5 Incident photon-to-current conversion efficiencies of QDSSCs based on the polymer electrolytes and stability test

Fig. 5a shows the IPCE spectra of QDSSCs prepared with liquid S/Na₂S electrolyte and PEO-PVDF polymer electrolytes with S/TMAS [M(S) = 0.02 M, S/TMAS molar ratio = 3] and S/Na₂S [M(S) = 0.02 M, S/Na₂S molar ratio = 3] redox additives. It can be seen that, compared to the cell prepared with the liquid electrolyte, the solid-state QDSSCs prepared with the polymer electrolytes exhibit comparable or improved IPCE performance, and the cell prepared with the PEO-PVDF-S/TMAS electrolyte especially shows much higher IPCE

in the wavelength region of 340 - 550 nm. Fig. 5b shows the IPCE spectra of the QDSSCs prepared with the PEO-PVDF-S/TMAS electrolytes with different S/TMAS molar ratios, and the inset shows the maximum IPCE of the cells at 340 nm as a function of the S/TMAS molar ratio. It can be seen from this figure that increasing the S/TMAS molar ratio from 0.3 to 3 leads to a substantial increase in the maximum IPCE value, however further increasing this ratio beyond 3 causes a decrease in the IPCE value. This observation is consistent with the ionic conductivity measurement result that is shown in Fig. 3b. As reported previously, higher ionic conductivity generally corresponds to faster ion transport in the electrolyte, which facilitates the redox cycle and results in higher IPCE [33, 34].

Stability tests were also conducted to compare the performance of the QDSSCs prepared with liquid and polymer electrolytes. Fig. 5c shows the normalized IPCE of the QDSSC prepared with the liquid S/Na₂S electrolyte, while Fig. 5d shows the normalized IPCE of the cell prepared with the PEO-PVDF-S/TMAS electrolyte with an S/TMAS molar ratio of 3, and the insert in Fig. 5d shows the normalized IPCE at 340 nm as a function of the aging time. It can be seen that the normalized IPCE of the QDSSC prepared with the liquid electrolyte exhibits an almost 100% decrease after 75 min, while the cell prepared with the polymer electrolyte keeps 60% of its initial IPCE efficiency even after 245 h testing under same conditions. It is clear that the stability of the QDSSC is significantly improved by using the polymer electrolyte with the S/TMAS redox additive.

4. Conclusions

In this work polymer electrolytes based on PEO-PVDF with S/TMAS and S/Na₂S redox additives are investigated. UV-Vis and ionic conductivity measurements are performed to characterize their optical and electrochemical properties. QDSSCs are fabricated using the polymer electrolytes, and a possible additional redox process in the cells is proposed. The QDSSCs with the PEO-PVDF-S/TMAS electrolytes exhibit improved IPCE and device stability compared to the cell with liquid electrolyte. This research could provide important insights into the study of novel polymer electrolytes for energy harvesting and storage applications.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-10ER46728.

References

- [1] P. Ardalan, T.P. Brennan, H. Lee, J.R. Bakke, I. Ding, M.D. McGehee, S.F. Bent, *ACS Nano* 5 (2011) 1495.
- [2] I.K. Ding, N. Tetreault, J. Brillet, B.E. Hardin, E.H. Smith, S.J. Rosenthal, F. Sauvage, M. Grätzel, M. McGehee, *Adv. Funct. Mater.* 19 (2009) 2431.
- [3] H. Lee, H.C. Leventis, S. Moon, P. Chen, S. Ito, S.A. Haque, T. Torres, F. Nüesch, T. Geiger, S.M. Zakeeruddin, M. Grätzel, M. Nazeeruddin, *Adv. Funct. Mater.* 19 (2009) 2735.
- [4] J. Kang, W. Li, X. Wang, Y. Lin, X. Xiao, S. Fang, *Electrochim. Acta*, 48 (2003) 2487.
- [5] A.F. Nogueira, C. Longo, M.A. De Paoli, *Coord. Chem. Rev.* 248 (2004) 1455.
- [6] Z. Yu, Q. Zhang, D. Qin, Y. Luo, D. Li, Q. Shen, T. Toyoda, Q. Meng, *Electrochem. Commun.* 12 (2010) 1776.
- [7] P.V. Kamat, *Adv. Funct. Mater.* 19 (2009) 805.
- [8] J.A. Chang, J.H. Rhee, S.H. Im, Y.H. Lee, H. Kim, S.I. Seok, M.K. Nazeeruddin, M. Grätzel, *Nano Lett.* 10 (2010) 2609.
- [9] V. Chakrapani, K. Tvrđy, P.V. Kamat, *J. Am. Chem. Soc.* 132 (2010) 1228.
- [10] P.V. Kamat, K. Tvrđy, D.R. Baker, J.G. Radich, *Chem. Rev.* 110 (2010) 6664.
- [11] Y.L. Lee, Y.S. Lo, *Adv. Funct. Mater.* 19 (2009) 604.
- [12] Y.L. Lee, C.H. Chang, *J. Power Sources* 185 (2008) 584.
- [13] Y. Tachibana, H.Y. Akiyama, Y. Ohtsuka, T. Torimoto, S. Kuwabata, *Chem. Lett.* 36 (2007) 88.
- [14] H.K. Jun, M.A. Careem, A.K. Arof, *Renew. Sust. Energ. Rev.* 22 (2013) 148.
- [15] Q. Dai, J. Chen, L. Lu, J. Tang, W. Wang, *App. Phy. Lett.* 102 (2013) 203904.
- [16] L. Li, X. Yang, J. Gao, H. Tian, J. Zhao, A. Hagfeldt, L. Sun, *J. Am. Chem. Soc.* 133 (2011) 8458.
- [17] S. Wang, Q.X. Zhang, Y.Z. Xu, D.M. Li, Y.H. Luo, Q.B. Meng, *J. Power Sources* 224

323 (2013) 152.
 324 [18] A.K. Safyan, *Int. J. Electrochem. Sci.* 7 (2012) 561.
 325 [19] N.S.A. Manan, L. Aldous, Y. Alias, P. Murray, L.J. Yellowlees, M.C. Lagunas, C.
 326 Hardacre, *J. Phys. Chem. B* 115 (2011) 13873.
 327 [20] W.F. Giggenbach, *Inorg. Chem.* 3 (1974) 1730.
 328 [21] K.Y. Chen, J.C. Morris, *Environ. Sci. Technol.* 6 (1972) 529.
 329 [22] K.Y. Chen, J.C. Morris, *Advances in water pollution research*, 5th International
 330 Conference on Water Pollution Research, San Francisco, USA, July 27-30, 1970; S.H.
 331 Jenkins, Ed.; Pergamon Press: Oxford, New York, 1972.
 332 [23] D. Zhao, H. Ren, J. Wang, Y. Yang, Y. Zhao. *Energ. Fuel* 21 (2007) 2543.
 333 [24] W. Giggenbach, *Inorg. Chem.* 7 (1971) 1333.
 334 [25] V. Chakrapani, D. Baker, P.V. Kamat, *J. Am. Chem. Soc.* 133 (2011) 9607.
 335 [26] J.B. Lee, *Electrochemistry of FeSO₄-Na₂S₂O₃ and CuSO₄-Na₂S₂O₃ Systems for*
 336 *Template-Assisted Nanowire Synthesis*. Ph. D. Thesis, University of California, Berkeley,
 337 Fall, 2011.
 338 [27] Y. Yang, C. Zhou, S. Xu, H. Hu, B. Chen, J. Zhang, S. Wu, W. Liu, X. Zhao, *J. Power*
 339 *Sources* 185 (2008) 1492.
 340 [28] J. P. Sharma, S.S. Sekhon, *Solid State Ionics* 178 (2007) 439.
 341 [29] Y. Yang, J. Zhang, C. Zhou, S. Wu, S. Xu, W. Liu, H. Han, B. Chen, X.Z. Zhao, *J. Phys.*
 342 *Chem. B* 112 (2008) 6594.
 343 [30] M. Malchus, M. Jansen, *Acta Cryst. B* 54 (1998) 494.
 344 [31] B. Scholarly, *Sulfuric acids—advances in research and application*, Acton, Q. A. Scholarly
 345 Edition: Atlanta, Georgia, 2013; pp 7-8.
 346 [32] J. J. Whiting, *The Chemistry of Compounds Containing N–O and N–S Bonds*, Ph.D.
 347 Thesis, McGill University, July, 1970.

- 348 [33]M. Kang, K. Ahn, J. Lee, J. Power Sources 180 (2008) 896.
- 349 [34] S. Yang, H. Kou, H. Wang, K. Cheng, J. Wang, New J. Chem.34 (2010) 313.
- 350

Figure captions:

Fig. 1. SEM images of PEO-PVDF polymer electrolytes with (a) S/TMAS and (b) S/Na₂S redox additives.

Fig. 2. UV-Vis spectra of the PEO-PVDF polymer electrolytes: (a) With pure S, S/TMAS [S/TMAS molar ratio = 3, M(S) = 0.02 M], and S/Na₂S [S/Na₂S molar ratio = 3, M(S) = 0.02 M]. The insert shows the enlarged PEO-PVDF-S/Na₂S spectrum. (b) With different S/TMAS molar ratios. The insert shows the dependence of the absorption intensity on S/TMAS molar ratio.

Schematic 1. Schematic of the redox process in solid-state QDSSCs based on PEO-PVDF polymer electrolyte with S/TMAS.

Fig. 3. Ionic conductivity of the PEO-PVDF polymer electrolytes (a) with different redox additives and (b) with different S/TMAS molar ratios.

Fig. 4. ATR-FTIR spectra of the PEO-PVDF, PEO-PVDF-S, PEO-PVDF-TMAS, PEO-PVDF-S/Na₂S (S/Na₂S molar ratio = 3), and PEO-PVDF-S/TMAS with different S/TMAS molar ratios in the wavelength range of (a) 4000 - 400 cm⁻¹, (b) 1050 - 910 cm⁻¹, and (c) 650 - 550 cm⁻¹.

Fig. 5. (a) IPCE spectra of the QDSSCs with PEO-PVDF polymer electrolytes with different redox additives and a liquid electrolyte with S/Na₂S. (b) IPCE spectra of the QDSSCs with PEO-PVDF-S/TMAS polymer electrolytes with different S/TMAS molar ratios. The insert shows the maximum IPCE value at 340 nm as a function of the S/TMAS molar ratio. (c) Normalized IPCE of the QDSSC with 1 M liquid S/Na₂S electrolyte. (d) Normalized IPCE of the QDSSC with the PEO-PVDF-S/TMAS polymer electrolyte with an S/TMAS molar ratio of

373 3. The insert shows the normalized IPCE at 340 nm as a function of the aging time.

Fig. 1

Fig. 2

Schematic 1

Fig. 3

Fig. 4

Fig. 5