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Lindqvist polyoxometalates as electrolytes in p-type dye sensitized solar cells†

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The development of new redox couples provides a clear strategy to improve power conversion efficiency (PCE) in p-type dye-sensitized solar cells (p-DSSCs) through enabling improvements in open-circuit voltage (V_{OC}). In this work we report the use of molybdenum and tungsten containing Lindqvist polyoxometalates (POMs), $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$, as an alternative to the traditionally used I^-/I_3^- redox mediator in p-DSSCs. POM electrolytes are cheap and easy to synthesize, air stable and transparent, making them suitable for tandem solar cell applications. Electrolytes were evaluated using a simple testing device to benchmark the respective devices. Up to a 5-fold increase in V_{OC} was observed for p-DSSCs employing electrolytes with POMs upon comparison with traditionally used I_3^-/I^- , while short-circuit photocurrents with the same order of magnitude were observed under identical dilute conditions.

Introduction

With an ever increasing energy demand and the prospect of climate change as a consequence of greenhouse gas emission, alternatives to fossil fuels are needed. Solar energy has the most potential for providing this energy in a sustainable fashion.¹ Dye-sensitized solar cells (DSSCs) are considered as a promising low-cost alternative to traditional crystalline silicon solar cells.² Furthermore, they can be made from sustainable materials and can absorb diffuse light, making them suitable for small scale appliances.^{3,4}

n-Type DSSCs based on mesoporous TiO_2 have achieved an efficiency of 11.9% with traditional iodide electrolytes, with greater power conversion efficiencies (PCEs) made possible through the use of alternative redox couples, enabling PCE improvements through increases in open-circuit voltage (V_{OC}) without sacrificing short-circuit photocurrent (J_{SC}).^{5–8} Complementary improvements in p-type DSSCs (p-DSSC), based on

mesoporous NiO semiconductors, aim to enable the fabrication of highly efficient tandem DSSC devices. However, p-DSSCs exhibit much lower PCEs than n-type DSSCs.^{9–12}

Besides engineering the mesoporous semiconductor and dye of the p-DSSC, the development of the redox mediator within the electrolyte of the p-DSSC provides a clear pathway to device optimization, as evidenced by several groups using cobalt pyridyl complexes,^{13,28} disulfides/thiolates,¹⁴ cobalt diaminoethane complexes¹⁵ and iron acetylacetonate complexes.¹⁶ Traditionally used I_3^-/I^- couples have been scrutinized due to their ambiguous mechanism as an electrolyte and parasitic absorption of visible light. The absorption of visible light by the I_3^-/I^- couple removes photons utilizable by the dye, reducing J_{SC} , while the radical $I_2^{\cdot-}$ formed upon visible light excitation, recombines with a photogenerated hole at the semiconductor–electrolyte interface,¹⁷ compromising the V_{OC} of the device. Importantly, devices based on I_3^-/I^- electrolytes suffer from low V_{OC} , as their redox potential is not energetically matched in an optimal fashion with the optoelectronic properties of the dye. The redox potential of the I_3^-/I^- electrolyte also limits its solar fuel applications, to drive for example CO_2 -reduction catalysts.

Bach *et al.* demonstrated an elegant solution to improving V_{OC} in p-DSSCs by employing $[Co(en)_3]^{3+/2+}$ and $[Fe(acac)_3]^{0/1-}$ redox mediators that exhibit higher redox potentials than I_3^-/I^- couples, enabled by appropriate matching of dye electronics, leading to higher PCEs.^{13–16} It is important to note that the increase in redox potential is solely beneficial for p-type DSSCs and not for tandem cells. The cobalt and iron based electrolytes are however unstable in air and therefore have to be prepared under inert conditions, complicating device fabrication. Also, the cobalt and iron based electrolytes compete for visible light absorption with the dyes, making them less suitable for tandem solar cell applications.

Polyoxometalates (POMs) are well-known anionic metal oxide clusters that can host several heteroatoms.¹⁸ POMs are widely used because of their electrochemical properties. Recent applications included water oxidation catalysts, as components in redox flow batteries, lithium ion batteries and super

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capacitors.^{19–22} POMs have also been used as co-adsorbents on NiO surfaces in p-type DSSCs, which showed a decreased recombination rate and increased V_{OC} .²³ To our knowledge, POMs have not been employed as redox mediators in p-DSSCs.

In this work we report the use of Lindqvist polyoxometalates (POMs) as electrolytes for p-type DSSCs. Lindqvist POMs have a molecular formula $M_6O_{19}^{2-}$ and spherical shape. As we are particularly interested in the development of p-type DSSCs with higher V_{OC} for the realization of solar fuel devices, a simple testing device was constructed to enable rapid optimization (Fig. 6).

Results and discussion

The Lindqvist POMs used in this work are $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$. The structure of a typical Lindqvist POM is depicted in Fig. 1.

The POMs were synthesized *via* two simple procedures as previously described by Fournier and Wang *et al.*, with the characterization of the POM structure achieved by single crystal X-ray diffraction.²⁴ The POMs have been made from cheap starting materials, employing abundant elements coupled with air stability, making them amenable to scale-up. The $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$ POMs demonstrated respective solubilities of 21 g L⁻¹ and 67 g L⁻¹ in acetonitrile, limiting their application in DSSCs. The acetonitrile solution of $[TBA]_2Mo_6O_{19}$ afforded a faintly yellow solution and $[TBA]_2W_6O_{19}$ yielded a clear solution. As shown in Fig. 2, the molar absorption coefficients of both POMs are over 100 times lower than that of the traditional I_3^-/I^- electrolyte.

A combination of cyclic voltammetry and differential pulse voltammetry was employed to determine the redox potential, reversibility and diffusion coefficient of both POMs. Fig. 3 shows the differential pulse voltammogram of both POMs, which exhibit respective redox potentials of -0.40 V and -0.90 V (*vs.* NHE) for $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$. The experiments were performed under aerobic conditions,

Fig. 1 Typical Lindqvist $M_6O_{19}^{2-}$ polyoxometalate with the metal atoms depicted in orange and the oxygen atoms depicted in red.

Fig. 2 Extinction coefficient spectra of $[TBA]_2W_6O_{19}$, $[TBA]_2Mo_6O_{19}$ and I_3^-/I^- in acetonitrile, with the inset showing the difference between of $[TBA]_2W_6O_{19}$ and $[TBA]_2Mo_6O_{19}$. Concentration of $[TBA]_2W_6O_{19}$, $[TBA]_2Mo_6O_{19}$ and I_3^-/I^- was 1.7×10^{-5} M, 3.5×10^{-5} M and 1.7×10^{-7} M for $[TBA]_2W_6O_{19}$, $[TBA]_2Mo_6O_{19}$ and I_3^-/I^- respectively.

showing the air stability of the POMs. The broad peak separation in the cyclic voltammetry experiments and the bell shaped curve in the differential pulse voltammogram experiments can be explained by the fact that no supporting electrolyte was used and the experiments were done in acetonitrile (see the ESI†).

Given that the redox potential of I_3^-/I^- , $[Co(en)_3]^{3+/2+}$ and $[Fe(Acac)_3]^{0/1-}$ is reported to be +0.32 V, -0.03 V and -0.20 V *vs.* NHE respectively,¹⁶ the $[TBA]_2W_6O_{19}$ POM demonstrates the lowest redox potential to our knowledge. The low redox potential of $[TBA]_2W_6O_{19}$ should translate into an elevated V_{OC} in the p-DSSC device, making the POMs an excellent candidate as a redox mediator. Fig. 4 shows an energy level diagram of the components in the p-type DSSCs used in this work. The LUMO of the P1 dye has been reported to be around -0.93 V *vs.* NHE.^{11,25} This means that there is 0.03 V available for electron transfer from the dye to the redox mediator in the case of $[TBA]_2W_6O_{19}$. Although this should be enough energy to regenerate the $[TBA]_2W_6O_{19}$ POM, a low J_{SC} can be expected as

Fig. 3 Differential pulse voltammogram of $[TBA]_2Mo_6O_{19}$ and $[TBA]_2W_6O_{19}$ saturated solution in acetonitrile using a glassy carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode.

Fig. 4 Energy-level diagram of the semiconductor, P1-dye and redox couples used in this work.

the driving force is very small, reducing the rate of this electron transfer process. In the case of $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ there is 0.53 V of driving force available, which should afford lower V_{OC} values than those of the $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ POM, but higher J_{SC} values.

Fig. 5 Scan rate dependent cyclic voltammetry with a glassy carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode of (a) $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ and (b) $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$. Conversion of potential vs. Ag/AgCl to the NHE is given in the ESI.†

Cyclic voltammetry presented in Fig. 5 demonstrates that both POMs are electrochemically reversible. The scan-rate dependent measurements provide information on the diffusion constants of the different POMs.¹⁶ Using the Randles-Sevcik equation, the electrochemical data show that $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ and $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ have a diffusion coefficient of $2.02 (\pm 0.35) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $1.08 (\pm 0.09) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ respectively. Earlier studies with the $[\text{Fe}(\text{acac})_3]^{0/1-}$ electrolyte revealed that this species demonstrates a diffusion coefficient of $7.1 (\pm 0.78) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.¹⁶ It was also reported that the J_{SC} was limited by diffusion, a well-known phenomenon observed when employing redox mediators with greater size.¹⁶ Since the POMs in this work feature lower diffusion coefficients, it is likely that the J_{SC} of the corresponding p-DSSCs will experience diffusion limitations.

We designed and fabricated a simple device to specifically measure the V_{OC} in a simple and expedient manner. The device is made from a screen-printed NiO photocathode (1.57 cm^2) on FTO glass, subsequently sensitized with the frequently used P1 dye.^{25–27} As depicted in Fig. 6, the counter electrode was made from platinum coated FTO. In the device the two electrodes are separated by a 1 cm distance by a Teflon container, featuring a large opening at the top to facilitate the introduction and removal of electrolyte solutions, and washing of the system. The Teflon container has a volume of 3 mL of electrolyte solution. It is expected that the increased distance between the electrodes will amplify diffusion limitations in the system, leading to lower J_{SC} , but it allows the benchmarking of the V_{OC} of various devices in an expeditious manner.²⁹

Table 1 summarizes the photovoltaic parameters obtained from the measurement of the J - V properties of the DSSCs. The POM electrolytes are compared with the I_3^-/I^- electrolyte at

Fig. 6 Simple testing device used in this work to benchmark the open current voltage. Design schematics of the device are shown in the ESI.†

Table 1 Photovoltaic parameters of the p-type DSSCs prepared in this work. Data were obtained from I - V curve measurements performed under AM1.5 solar irradiation (100 mW cm^{-2})

Entry	Electrolyte	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF
1	0.01 M $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ ^a	423 ± 28	0.021 ± 0.002	0.13 ± 0.02
2	0.01 M $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ ^a	541 ± 34	0.010 ± 0.001	0.11 ± 0.02
3	0.01 M I_3^-/I^- ^a	100 ± 5	0.032 ± 0.003	0.23 ± 0.01
4	1.0 M I_3^-/I^-	144 ± 14	0.107 ± 0.013	0.31 ± 0.02
5	1.0 M I_3^-/I^- (literature) ²⁶	106	3.010	0.37
6	$\text{Co}(\text{tbp})_3$ (literature) ²⁷	80	0.26	0.26

^a 0.5 M of LiTFSI was present as the supporting electrolyte. The data shown are the average and the standard deviation of at least 5 different experiments.

a reduced concentration (0.01 M as opposed to 1.0 M) due to the limited solubility of the POM materials in MeCN. Interestingly, devices based on the POM electrolytes (entries 1 & 2) show a dramatic increase in V_{OC} compared the I_3^-/I^- couple (entry 3), corresponding clearly to the differences in redox potentials measured from electrochemical characterization. Also, the elevated V_{OC} of $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ compared to $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ is consistent with the slightly higher oxidation potential of $[\text{TBA}]_2\text{W}_6\text{O}_{19}$. Comparing the two POM-electrolyte devices, the lower J_{SC} of the $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ device (entry 1) can be explained by either the smaller driving force for the reduction of $[\text{TBA}]_2\text{W}_6\text{O}_{19}$ by the photoreduced dye compared to $[\text{TBA}]_2\text{Mo}_6\text{O}_{19}$ or the greater diffusion coefficient. Given that the J_{SC} values of all devices have the same order of magnitude when low concentration redox mediators are utilized, the POM materials are promising candidates as electrolytes for p-type DSSCs. Wu *et al.* showed the impact of the electrolyte recombination resistance on the fill factor.³⁰ It is likely that this is also the cause of the low fill factor in this system. The results in Table 1 also show the effect of increasing the concentration of the electrolyte (entries 3 and 4), when using the I_3^-/I^- couple. Both the V_{OC} and the short-circuit current increase when the concentration is higher. Since the solubility of the POMs in acetonitrile is low, similar experiments with these electrolytes are not possible. Clearly, more soluble analogues are required for practical applications.

The effectiveness of the simple test cell is clear when comparing our results with those reported in the literature. The V_{OC} obtained for the test cell are similar to those reported in the literature (entries 4 and 5), and only the J_{SC} is lower as a result of the large distance between the electrodes. Given the fact that it is really easy to change the electrolyte solution, the test cell is very suitable for benchmarking V_{OC} .

Conclusions

We have shown that polyoxometalates can be used as electrolytes in p-type dye sensitized solar cells. The POMs presented in this work are easy to prepare based on cheap starting materials. A unique feature of these POMs as electrolytes is that they are transparent and can therefore be suitable for tandem solar cell applications. An increased V_{OC} is not directly beneficial to tandem solar cell applications, but may be useful for pure p-type

solar cells. The POMs are also air stable, allowing for easy preparation of the electrolyte and the DSSC. We also report a simple testing setup that allows us to benchmark the open current potential for different devices thereby facilitating the optimization of electrolyte solutions.

In line with what we expected on the basis of the redox potentials of the POM materials, measured by electrochemistry, we found a 4 to 5-fold increase in V_{OC} when applying these POM electrolytes in comparison to the devices with the traditional I_3^-/I^- couple. We plan to exploit these voltages in proton and CO_2 reduction for solar fuel applications. The high V_{OC} is sufficient to drive proton reduction catalysis and CO_2 reduction catalysis. The J_{SC} have the same order of magnitude under the same conditions. Currently, the low solubility of the POMs is the main hampering factor for increasing the short-circuit current of these cells. Increasing the solubility of these POM materials should therefore be the main focus point when improving the efficiency of these cells. After solubility issues are fixed, traditional DSSCs can be made in order to achieve record efficiencies.

Conflicts of interest

There are no conflicts to declare.

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