Aqueous Biphasic Dye-Sensitized Photosynthesis Cells for TEMPO-Based Oxidation of Glycerol

Bruggeman, D.F.; Laporte, A.A.H.; Detz, R.J.; Mathew, S.; Reek, J.N.H.

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Abstract: This work reports an aqueous dye-sensitized photoelectrochemical cell (DSPEC) capable of oxidizing glycerol (an archetypical biobased compound) coupled with H₂ production. We employed a mesoporous TiO₂ photoanode sensitized with the high potential thienopyrrololedione-based dye AP11, encased in an acetonitrile-based redox-gel that protects the photoanode from degradation by aqueous electrolytes. The use of the gel creates a biphasic system with an interface at the organic (gel) electrode and aqueous anolyte. Embedded in the acetonitrile gel is 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), acting as both a redox-mediator and a catalyst for oxidative transformations. Upon oxidation of TEMPO by the photoexcited dye, the in situ generated TEMPO⁺ shuttles through the gel to the acetonitrile–aqueous interface, where it acts as an oxidant for the selective conversion of glycerol to glyceraldehyde. The introduction of the redox-gel layer affords a 10-fold increase in the conversion of glycerol compared to the purely aqueous system. Our redox-gel protected photoanode yielded a stable photocurrent over 48 hours of continuous operation, demonstrating that this DSPEC is compatible with alkaline aqueous reactions and used for energy-intensive applications, including transport and metal refining. Dye-sensitized photoelectrochemical cells (DSPECs) are an extension of dye-sensitized solar cells (DSSCs) and produce fuel instead of electricity by introducing catalytic redox reactions at the respective electrodes within the device. DSSCs use molecular dyes, wide-band gap semiconductors, and redox-mediators to absorb the light that facilitates a solar-to-electrical energy conversion. Redox-mediators, responsible for dye regeneration in DSSCs, can be substituted for catalysts in DSPECs to realize catalytic chemical conversions. The majority of DSPECs involve water-splitting and generate hydrogen gas (H₂) as a potential valuable combustible fuel and chemical feedstock, and oxygen gas (O₂) as a byproduct. Currently, the efficiencies of such water-splitting devices are still low (~1%). Partly, this is because the oxygen evolution reaction (OER) exhibits a high kinetic barrier, as water oxidation is a four-electron process. Therefore, there is an interest in exploring alternative oxidative reactions in DSPECs that preferably involve two-electron processes, e.g., alcohol oxidation at photoanodes. Other potential advantages of novel reactions include the wider scope of reaction conditions that become accessible, e.g., the solvent and additives used, which have been demonstrated to improve photovoltaic properties in DSSCs. The anodic co-valorization means that we can couple the production of commercially valuable compounds to H₂ as fuel, instead of producing O₂. Although the demand for such fine chemicals (and therefore the coupled H₂ production) is significantly smaller than that global consumption of fuels, the innate utility of both anodic and cathodic products might facilitate an earlier uptake of this technology. The sustainability of DSPEC-facilitated photosynthetic production is enhanced further if biomass-derived feedstocks are valorized by oxidative transformation. In this process, biomass is photochemically reformed to biofuels or fine chemicals through oxidation. A promising candidate for biomass valorization is glycerol, as the oxidized products find application in, for instance, cosmetics and the preparation of polyesters and adhesives. Current DSPEC designs are incompatible for glycerol conversion as the substrate is water-soluble and its oxidation requires alkaline (pH~8.5) conditions. The prerequisites for glycerol conversion causes stability issues at the photoanode as the ubiquitously employed carboxylic acid—the best performing anchoring group for dyes to metal oxides—is prone to cleavage under aqueous alkaline conditions leading to dye desorption. More importantly, the photovoltaic properties in aqueous dye-sensitized systems

Aqueous Biphasic Dye-Sensitized Photosynthesis Cells for TEMPO-Based Oxidation of Glycerol

Didjay F. Bruggeman, Annechien A. H. Laporte, Remko J. Detz, Simon Mathew, and Joost N. H. Reek*

Alternatives to the currently used fossil-based energy sources are urgently needed to sustain modern-day human society. Artificial photosynthesis seeks to address this goal with devices that produce chemical fuels using sunlight as energy input. In contrast to photovoltaic electricity, fuels can be stored at large scales to balance solar fluctuations and meet energy needs throughout the day. Although devices that produce chemical fuels using sunlight as energy input are an exciting area of research, many challenges remain before this technology can realize its full potential. One of the key challenges is the lack of suitable materials and devices that enable efficient and selective oxidation of water and biomass-derived feedstocks.

In this work, we describe an aqueous biphasic dye-sensitized photosynthesis cell (DSPEC) that can convert glycerol to glyceraldehyde. The cell utilizes a mesoporous TiO₂ photoanode sensitized with a high potential thienopyrroledione-based dye. The cell is encased in an acetonitrile-based redox-gel that protects the photoanode from degradation by aqueous electrolytes. The use of the gel creates a biphasic system with an interface at the organic (gel) electrode and aqueous anolyte. Embedded in the acetonitrile gel is 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), acting as both a redox-mediator and a catalyst for oxidative transformations. Upon oxidation of TEMPO by the photoexcited dye, the in situ generated TEMPO⁺ shuttles through the gel to the acetonitrile–aqueous interface, where it acts as an oxidant for the selective conversion of glycerol to glyceraldehyde. The introduction of the redox-gel layer affords a 10-fold increase in the conversion of glycerol compared to the purely aqueous system. Our redox-gel protected photoanode yielded a stable photocurrent over 48 hours of continuous operation, demonstrating that this DSPEC is compatible with alkaline aqueous reactions and used for energy-intensive applications, including transport and metal refining.

Dye-sensitized photoelectrochemical cells (DSPECs) are an extension of dye-sensitized solar cells (DSSCs) and produce fuel instead of electricity by introducing catalytic redox reactions at the respective electrodes within the device. DSSCs use molecular dyes, wide-band gap semiconductors, and redox-mediators to absorb the light that facilitates a solar-to-electrical energy conversion. Redox-mediators, responsible for dye regeneration in DSSCs, can be substituted for catalysts in DSPECs to realize catalytic chemical conversions. The majority of DSPECs involve water-splitting and generate hydrogen gas (H₂) as a potential valuable combustible fuel and chemical feedstock, and oxygen gas (O₂) as a byproduct. Currently, the efficiencies of such water-splitting devices are still low (~1%). Partly, this is because the oxygen evolution reaction (OER) exhibits a high kinetic barrier, as water oxidation is a four-electron process. Therefore, there is an interest in exploring alternative oxidative reactions in DSPECs that preferably involve two-electron processes, e.g., alcohol oxidation at photoanodes. Other potential advantages of novel reactions include the wider scope of reaction conditions that become accessible, e.g., the solvent and additives used, which have been demonstrated to improve photovoltaic properties in DSSCs. The anodic co-valorization means that we can couple the production of commercially valuable compounds to H₂ as fuel, instead of producing O₂. Although the demand for such fine chemicals (and therefore the coupled H₂ production) is significantly smaller than that global consumption of fuels, the innate utility of both anodic and cathodic products might facilitate an earlier uptake of this technology. The sustainability of DSPEC-facilitated photosynthetic production is enhanced further if biomass-derived feedstocks are valorized by oxidative transformation. In this process, biomass is photochemically reformed to biofuels or fine chemicals through oxidation. A promising candidate for biomass valorization is glycerol, as the oxidized products find application in, for instance, cosmetics and the preparation of polyesters and adhesives. Current DSPEC designs are incompatible for glycerol conversion as the substrate is water-soluble and its oxidation requires alkaline (pH~8.5) conditions. The prerequisites for glycerol conversion causes stability issues at the photoanode as the ubiquitously employed carboxylic acid—the best performing anchoring group for dyes to metal oxides—is prone to cleavage under aqueous alkaline conditions leading to dye desorption. More importantly, the photovoltaic properties in aqueous dye-sensitized systems...
Typically compare poorly with systems using an organic solvent like acetonitrile,\textsuperscript{[25]} incurring losses in power conversion efficiency, lower injection efficiency and shifts of conduction band levels.\textsuperscript{[26]} To make the DSPEC compatible with alkaline aqueous phase conditions required for glycerol oxidation, we envision a biphasic DSPEC system in which the photoanode is protected by an organic phase gel layer. As such, the oxidative reaction takes place in the aqueous phase while an efficient solvent environment for the photoanode (e.g., acetonitrile) is maintained.

The biphasic DSPEC (Scheme 1) reported in this communication consists of a mesoporous TiO$_2$ photoanode on FTO (fluorine-doped tin oxide), sensitized with the high oxidation potential thienopyrroledione-based dye AP11\textsuperscript{[26]} 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) is a clear choice for the redox-mediating catalyst because 1) its redox-mediating ability in quasi-solid DSSCs using acetonitrile-poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) gel electrolytes\textsuperscript{[27]} 2) it can act as a redox-mediating catalyst in acetonitrile-based DSPECs\textsuperscript{[15, 28]} and 3) TEMPO\textsuperscript{+} has been utilized for the selective aqueous (pH \approx 8.5) chemical oxidation of glycerol to glyceraldehyde\textsuperscript{[16, 22, 29]} We created a biphasic system device by applying the acetonitrile-based PVDF-HFP gel\textsuperscript{[27]} over the dye-sensitized photoanode, protecting it from aqueous reaction conditions that lead to device deactivation. Gel-embedded TEMPO can regenerate photooxidized AP11 at the dye-semiconductor interface, generating TEMPO\textsuperscript{+} that can diffuse through the gel to reach the gel-aqueous interface to facilitate glycerol oxidation. As shown by our previous work, it is crucial that in situ photogenerated TEMPO\textsuperscript{+} must migrate away from the semiconductor surface to prevent recombination.\textsuperscript{[29]} Thus, our envisioned biphasic DSPEC design will only function if the TEMPO redox-mediating catalyst resides in the organic-gel layer. The photogenerated TEMPO\textsuperscript{+} should diffuse sufficiently fast to the interface to perform the chemical oxidation reaction. Lastly, the gel must not degrade under the employed reaction conditions.

Control experiments were performed to assess the ability of a TEMPO(BF$_4$)$^{\text{3+}}$ loaded gel to oxidize glycerol in a biphasic system with glycerol residing in the aqueous layer. The TEMPO$^+$ in this experiment was used to emulate photogenerated TEMPO$^+$ in the envisioned DSPEC. At the same time, the gel stability and the substrate/product distribution over the different layers were probed after 16 hours of reaction time. All acquired experimental samples containing substrates and/or products in respective aqueous/organic solutions were TMS-derivatized prior to analysis by GC\textsuperscript{[32, 33]} We found that the TEMPO$^{\text{3+}}$ strongly preferred (Table 1, Entry 1, 97 \%) to remain in the gel phase. This behavior was independent of the gel layer thicknesses (Table S3, S4). The glycerol substrate and glyceraldehyde product (Table 1, Entries 2 and 3) demonstrated complementary solubility, with 85 \% and 87 \% residing in the aqueous phase, respectively. The orthogonal solubility of components in this system—redox-mediator in acetonitrile, substrate/product in aqueous—also simplifies product retrieval. Importantly, while these components are mainly in separate phases, efficient selective chemical oxidation of glycerol in the gel–aqueous solution was confirmed, with only a \approx 50 \% decrease in conversion (16.2 \%) compared to a fully homogeneous mixed reaction mixture (29.8 \%). We found that the gel stayed intact, and the system remained biphasic over several days, easily accommodating the 23 to 48-hour time-course of DSPEC experiments (see below). As such, the PVDF-HFP gel system displays the desired properties to construct the biphasic DSPEC (for more details, see Supporting Information, Table S2–S5)\textsuperscript{[32, 33]} Notably, substrates that show a preference for organic layers are proven to be not suitable for such a system (Table S7 and S8).

Preliminary experiments revealed that a minimum redox-gel thickness of 3 mm over the photoanode is needed in the DSPECs to obtain an even, reproducible and stable gel layer coverage over the entire surface of the photoanode. Therefore, the impact of gel layer thickness on the photovoltaic properties was assessed in sandwich-cell quasi solid-

$$\text{Table 1: Overview of the relative distribution over a 1:1 biphasic system of glycerol (1 eq.) and TEMPO(BF}_4\text{) (1.5 eq.) and conversion of glycerol to glyceraldehyde by TEMPO(BF}_4\text{) at }t=16\text{ hours. Biphasic systems consist of TEMPO(BF}_4\text{) in the acetonitrile-based gel and glycerol in the aqueous layer. Conversion and distribution over various gel thickness are shown in Table S3. Data is analyzed with GC after TMS-derivatization.}$$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Gel phase [%]</th>
<th>Aqueous phase [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEMPO$^{\text{3+}}$</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Glycerol</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>Glyceraldehyde</td>
<td>13</td>
<td>87</td>
</tr>
</tbody>
</table>
state DSSCs using redox-gels to confirm sufficient (re)generation of the photooxidized dye and TEMPO+. These quasi solid-state DSSCs were compared to a typical DSSC based on acetonitrile-based TEMPO++ electrolyte. The construction of the sandwich DSSC is detailed in the Supporting Information and Figure S5, and the photovoltaic parameters under irradiation with the 100 mW cm−2 LED white light source (Figure S6) are presented in Table 2. A typical AP11-sensitized DSSCs (Table 2, Entry 1) featuring an acetonitrile liquid electrolyte exhibits a short-circuit photocurrent \( I_{sc} \) of 3.8 mA cm−2 and an open-circuit voltage \( V_{oc} \) of 0.62 V. Electrolyte substitution with the TEMPO-gel (Table 2, Entry 2) yielded a \( \approx \) 10% reduction in \( J_{sc} \) and minimal impact to \( V_{oc} \). Increasing the gel thickness from 60 μm to 1, 2 or 3 mm resulted in an approximately similar reduction of photovoltaic performance (Table 2, Entries 3–5). The DSSC with the redox-gel thickness of 3 mm experienced a reduction in \( J_{sc} \) to 2.6 mA cm−2 (from 3.8 mA cm−2) while the \( V_{oc} \) reduced to 0.41 V (from 0.61 V). The lower performance is a result of increased distance between the electrodes leading to diffusion limitations and, as a result, increased recombination at the semiconductor–gel interface due to the accumulation of oxidized species at the photoanode, in line with what was previously reported. Furthermore, the gel increases cell resistance due to low ion diffusion that leads to a lower Fill Factor (FF). The combined effects contribute to a decrease in \( \eta \) for the 3 mm gel DSSC compared to the liquid 0.060 mm analog (by 70%). However, it still produces sufficient \( J_{sc} \) to generate TEMPO+ for glycerol oxidation in DSPECs. Importantly, future optimization may focus on the generation of devices with smaller gel layers.

Next, we explored the light-driven oxidation of glycerol to glyceraldehyde in a DSPEC. DSPECs were assembled with enlarged WEs (FTO | TiO2 | AP11, mask size 0.64 cm2) and CEs (FTO | Pt), which were prepared similar to the (photo-)electrodes used in DSSCs (see above). The electrodes were placed in a DSPEC photoreactor (Figure 1A) composed of two Teflon compartments (photoanodic for glycerol oxidation and cathodic for H2 production) separated by a Nafion-117 membrane. The redox-gel-containing the TEMPO (1.0 M) was (hot) drop-cast on the photoanode yielding a protective gel layer with a thickness of 3 mm. After the gelation was complete (\( \approx \) 0.5 hours), the anolyte containing 0.1 M glycerol was introduced (sat. NaCl, NaHCO3, pH 8.3, 3 mL; see Figure 1B). Chronoamperometric experiments were performed using the photoanode illuminated by the photoanode with a 100 mW cm−2 white LED (Figure S6) for 23 hours, using a small bias potential of 0.1 V vs. Ag/AgCl (Figure 7A). Aliquots of the anodic reaction mixture were TMS derivatized and analyzed by GC to probe the conversion, and the results are shown in Figure 2B and summarized in Table 3. Control experiments were performed using the redox-gel DSPEC without illumination, using a redox-gel DSPEC without TEMPO as a redox-mediating catalyst, and by using the DSPEC without gel.

The experiment where the biphasic redox-gel DSPEC system was irradiated for 23 hours (Table 3, Entry 1) yielded...
The DSPEC photoanodes and redox-gels were investigated after the experiments to gain insight into the stability of the device. The redox-gel preserved its bright orange color after 48 hours of chronoamperometric illumination (Figure 1C), consistent with the control experiments described in Table 1 that reveal only a small fraction (6 %) of all TEMPO was found in the aqueous layer samples (Figure S8). The water present in the gel layer only increased by 1 % (Table S6) after a 48-hour experiment. Qualitative and quantitative colorimetric analysis of FTO | TiO₂ | AP11 photoanodes (Figure 2A and Table S10) is performed, as the disappearance of the yellow color indicates detachment or decomposition of the AP11 dye due to the lingering of the dye in the oxidized state. DSPEC photoanodes featuring gel layers without the TEMPO redox-mediator were completely bleached (Table S10, Entry 3). As expected, slight desensitization of the photoanodes was noted, in line with cleavage of the carboxylic acid linker of the AP11 dye under alkaline aqueous conditions. Soaking studies were performed in the dark to avoid dye decomposition by over-illumination, to study the impact of alkaline aqueous conditions, and confirmed the leaching of AP11 of TiO₂ in such an environment (Table S9). Interestingly, the yellow color was retained in the photoanode protected with the redox-gel, indicating that the gel prevents cleavage of the dye, and there is sufficient redox-mediator in the gel system present to avoid the photodecomposition of the dye. Furthermore, the redox-gel based DSPEC still performs after 24 hours, whereas the fully aqueous-based DSPEC no longer generates photocurrent after ≈15 hours (Figure S7B).

Interestingly, the system needs several hours before the reaction proceeds with 100 % Faradaic efficiency. We surmise that the DSPEC builds up the TEMPO⁺ concentration in the gel based on the diffusion through the redox-gel layer to a steady-state required to allow oxidation reactions to occur at the gel-electrolyte interface. Therefore, we performed 48-hour experiments to confirm the steady-state in TEMPO⁺ and further probe the system’s stability. These experiments show (Figure S11–S13) that the DSPEC with a gel layer tends to stabilize after approximately 20 hours of irradiation, after which a stable photocurrent density of ≈0.18 mA cm⁻² is observed, producing glyceraldehyde with a near 100 % Faradaic efficiency. In a separate experiment, the redox-gel based DSPEC was illuminated for 7 hours to quantify the amount of H₂ formed during the experiment, and this experiment shows (Figures S9 and S10) a high Faradaic efficiency in H₂ formation (of ≈90 %). This experiment ultimately shows that the gel-protected biphasic DSPEC allows simultaneous fuel formation and glycerol oxidation.

In conclusion, we have demonstrated the selective light-driven TEMPO-mediated oxidation of glycerol to glyceraldehyde coupled to the production of H₂ in a biphasic DSPEC utilizing a gel-protected photoanode. The TEMPO redox-mediating catalyst is photooxidized to TEMPO⁺ in the acetonitrile-based gel and oxidizes glycerol at the gel–aqueous interface. The presence of the gel layer on the photoanode increases the photocurrent density and product formation by 10-fold compared to the aqueous DSPEC system. In the
absence of the gel layer, the photoanode decolorizes due to dye detachment under these conditions. The improved efficiency and high stability of the redox-gel-based DSPEC opens up the possibility for the photoconversion of other solely water-soluble including biomass-derived substrates such as cellulose, which also require relatively harsh conditions. Furthermore, product collection from the aqueous solution is improved thanks to the embedding of the active redox-mediating catalyst in the redox-gel. Most excitingly, the concept of employing a redox-gel to enhance the stability of aqueous DSPECs can be considered in the context of water-splitting DSPECs. On top of that, we are currently investigating if the redox-gel can prevent recombination in such cells by physically separating the water oxidation complex from the photoanode surface.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Biphasic Dye Sensitized Photoelectrochemical Cell · Hydrogen · Solar Fuel · Supramolecular Gel · TEMPO-Catalyzed Glycerol Oxidation