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*

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 thienopyrroledione-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 solutions 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-volatilization 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 of 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,[25] incurring losses in power conversion efficiency, lower injection efficiency and shifts of conduction band levels.[24] 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 oxidation 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.[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,[27] 2) it can act as a redox-mediating catalyst in acetonitrile-based DSPECs,[15, 28] and 3) TEMPO$^+$ has been utilized for the selective aqueous (pH$\approx$8.5) chemical oxidation of glycerol to glyceraldehyde,[16, 22, 29] We created a biphasic system device by applying the acetonitrile-based PVDF-HFP gel[27] over the dye-sensitized photoanode, protecting it from aqueous reaction conditions that lead to device deactivation. Gel-embedded TEMPO can regenerate photooxidized AP11 at the dye–semiconductor interface, generating TEMPO$^+$ 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$^+$ must migrate away from the semiconductor surface to prevent recombination.[30] Thus, our envisioned biphasic DSPEC design will only function if the TEMPO redox-mediating catalyst resides in the organic-gel layer. The photogenerated TEMPO$^+$ 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$_4$)$^{−}$[31] 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.[32, 33] We found that the TEMPO$^{+}$ 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 system 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). 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-

![Scheme 1: Schematic representation of an aqueous (blue) biphasic DSPEC containing redox-gel layer (yellow) for glycerol oxidation and simultaneous H$_2$ production. Proposed mechanism: 1) irradiation and excitation of a dye, 2) injection of e$^−$ in the TiO$_2$ CB, 3) e$^−$ moves to cathode, 4) TEMPO regenerates dye and is oxidized, 5) TEMPO$^+$ oxidizes glyceraldehyde to the gel–aqueous interface (green) 6) proton reduction to form hydrogen gas as fuel. D$^+$ = oxidized dye (1.8 V), D$^0$ = excited dye (~0.8 V), e$^−$ = electrons, CB = conduction band at ~0.5 V, TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO$^+$ = oxidized TEMPO, V vs. NHE.](image)

<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$^{+}$</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>
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</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 TEMPOκ+ 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 \( (J_\text{sc}) \) of 3.8 mA cm\(^{-2}\) and an open-circuit voltage \( (V_\text{oc}) \) of 0.62 V. Electrolyte substitution with the TEMPO-gel (Table 2, Entry 2) yielded a \( \approx 10\% \) reduction in \( J_\text{sc} \) and minimal impact to \( V_\text{oc} \). 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 \( J_\text{sc} \) to 2.6 mA cm\(^{-2}\) (from 3.8 mA cm\(^{-2}\)) while the \( V_\text{oc} \) reduced to 0.41 V (from 0.61 V). The lower performance is the result of increased resistance 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.\(^{3,4,30}\) 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%).\(^{30}\) However, it still produces sufficient \( J_\text{sc} \) 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 WEIs (FTO | TiO\(_2\) | AP11, masked size 0.64 cm\(^2\)) 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 H\(_2\) production) separated by a Nafion-117 membrane. The redox-gel containing the TEMPO (1.0 M) was (hot) drop-casted 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, NaHCO\(_3\), pH 8.3, 3 mL; see Figure 1B). Chronoamperometric experiments were performed by illuminating 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 S7A). 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. Quantitative and qualitative 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 [31].

### Figure 2

A) Images of used photoanodes in 23 hours DSPEC experiments, and B) GC quantification of light-driven glyceraldehyde production in a DSPEC with 3 mm TEMPO redox-gel layer (orange) and a full aqueous TEMPO-based system (blue) with the anticipated amount of glyceraldehyde based on photocurrent (redox-gel: brown, aqueous dark blue). The integration of half the photocurrent determines the number of electrons to account for two electrons needed per oxidation reaction. A bias potential of 0.1 vs. Ag/AgCl was applied on the WE and the system was illuminated with a 100 mW cm⁻² white LED light source (masked size 0.64 cm²). Experimental details are found Supporting Information and Table 3.

68.3 μmol of glyceraldehyde. This translates to a 100% Faradaic efficiency based on the photocurrent produced. Negligible photocurrent is produced in control experiments that exclude light or TEMPO (Figure S7B), and no glyceraldehyde was formed in these experiments as judged by GC analysis. As expected, both light and TEMPO are necessary to create an operational cell capable of the glycerol oxidation reaction (Table 3, Entries 2 and 3). The redox-gel DSPEC is compared to a fully aqueous DSPEC (Table 3, Entry 4 and Figure 2B), which contains a saturated solution of TEMPO (≈0.5 M). Although the TEMPO concentration is lower in the fully aqueous DSPEC, our previous studies have shown that DSPECs with TEMPO concentrations as low as 0.01 M in acetonitrile still work well and outperform the DSPEC based on the aqueous anolyte. [30] Furthermore, it is known that wettability issues for TEMPO-based aqueous electrolytes leading to poor pore infiltration are not an issue. [30] While both DSPECs—the TEMPO redox-gel and the completely aqueous redox system—demonstrate a Faradaic efficiency for glyceraldehyde production of ≈100%, the photocurrent produced by the TEMPO redox-gel based DSPEC is ≈10-fold higher than that of the aqueous system. In line with this, the improved photocurrent results in a 10-fold increase in glyceraldehyde production.

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 photocathode decolorizes due to
dye detachment under these conditions. The improved
efficiency and high stability of the redox-gel-based DSPECs
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.[17]
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
improved thanks to the embedding of the active redox-
gel. On top of that, we are currently investigat-

Glycerol Oxidation

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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.

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