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An oxygen-reducing biocathode with “oxygen tanks”

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Polytetrafluoroethylene submicro-rods, serving as micro-scaled “oxygen tanks” and binders, have been mixed into Os redox polymer-based bilirubin oxidase cathodes, leading to both enhanced limiting current density of oxygen reduction reaction in neutral pH and operational stability over 16 hours.

Enzymatic biofuel cells (EBFCs) relying on enzyme modified electrodes are of considerable interest, allowing the conversion of chemical energy into electricity¹. Their potential application as the powering unit of implantable² and wearable³ medical devices utilising endogenous sugars, such as glucose and lactate readily presenting in biofluids, makes EBFCs even more appealing. A typical EBFC is composed of a fuel-oxidising anode collecting electrons from the fuel using an enzyme catalyst and a cathode undergoing enzyme-catalysed oxygen reduction reaction (ORR)¹, although some researchers employ oxygen-derived H₂O₂ as the oxidant for the cathode^{4, 5, 6}. However, solubility of dioxygen in aqueous solution is quite limited (~1.2 mM maximum at neutral pH and 1 atm O₂; ~0.3 mM if equilibrated in air), and is considerably lower than the level of physiological glucose (3.3 and 4.8 mM in muscle and plasma⁷, respectively), not to mention that the dioxygen concentration *in vivo* is even lower (0.14 and 0.08 mM in arterial blood and intestinal tissue⁸, respectively). Thus, the ORR at the cathode is typically the limiting electrode of a glucose/O₂ EBFC^{9, 10}. Gas-breathing enzymatic cathodes could maintain oxygen concentration by steadily dissolving gaseous oxygen at a triple-phase boundary¹¹, but this approach is not suitable for implantable devices. Another strategy is to replace enzymatic cathodes with abiotic cathodes, which are typically transition metal based materials such as Prussian Blue¹², Ag₂O¹³ and MnO₂¹⁴, but these suffer from a depletion issue.

Recently Jeerapan et al. proposed an oxygen-rich cathode binder material, polychlorotrifluoroethylene (PCTFE), for Pt based cathodes¹⁵. The hydrophobic polymer binds molecular dioxygen, allowing the resultant hybrid biofuel cell to continuously generate power under an oxygen-free condition. Moreover, Zeng et al. employed a zirconium-based metal–organic framework, UiO-66-NO₂, as an oxygen “pump” to enrich oxygen for the ORR catalyst cobalt phthalocyanine operating in an alkaline solution¹⁶. Furnishing ORR catalysts with oxygen-enriching materials is an emerging approach for oxygen-reducing cathodes. To the best of our knowledge, combining such oxygen-enriching materials with oxygen reducing enzyme catalysts, such as bilirubin oxidase (BOx), on a cathode has not been reported to date.

In this communication, polytetrafluoroethylene (PTFE) submicro-rods (**Fig. 1**) are studied as “oxygen tanks” furnishing oxygen to a cathode comprised of an [Os(2,2'-bipyridine)₂(polyvinylimidazole)₁₀Cl]^{+/2+} (Os(bpy)₂PVI) (**Fig. S1A**) redox polymer co-immobilised using a poly(ethylene glycol)diglycidyl ether (PEGDGE) crosslinker^{17, 18} with BOx on a glassy carbon electrode (GCE) (**Scheme 1**). The Os(bpy)₂PVI also functions as the redox mediator facilitating electron transfer (ET) between BOx and GCE (**Fig. S1B**). In a mediated ET system, enzyme orientation on the electrode is not a key factor, making it simpler to implement. The PTFE submicro-rods (**Fig. 1**, length: 322±57 nm; diameter: 152±40 nm) adsorb dioxygen on the hydrophobic surface, thereby providing a higher local dioxygen concentration than that in aqueous solution¹⁹. PTFE has also been widely used in gas-breathing biocathodes

to tune the hydrophobicity/hydrophilicity balance at the interface¹¹. In addition, polymer coating onto a Os(bpy)₂PVI and lactate oxidase based electrode can improve redox polymer utilisation and thus increase electrochemical signal with high concentrations of lactate²⁰. Herein, two configurations of the cathode have been studied: i) forming a PTFE capping layer over the redox polymer/BOx layer (**Scheme 1B**) and ii) mixing PTFE within the redox polymer/BOx layer (**Scheme 1C**).

To prepare the cathode capped with PTFE, a cocktail solution containing Os(bpy)₂PVI, BOx and PEGDGE was first drop-cast onto

Fig. 1. SEM image of PTFE showing a rod-like morphology (A), measured rod diameter (B) and length (C).

Scheme 1. Schematic illustration of GCE supported redox polymer/BOx modified cathode (A), with a PTFE capping layer (B) or with mixed PTFE in the hydrogel (C).

the surface of GCEs (diameter: 4 mm), leading to GCE/Os(bpy)₂PVI-BOx (**Scheme 1A**, details in ESI[†]). Subsequently, 5 µl of 20% PTFE water suspension was drop-cast onto GCE/Os(bpy)₂PVI-BOx, resulting in GCE/Os(bpy)₂PVI-BOx/PTFE (**Scheme 1B**). **Fig. 2** compares cyclic voltammograms (CVs) of GCE/Os(bpy)₂PVI-BOx with and without PTFE capping. The GCE/Os(bpy)₂PVI-BOx displays a well-defined redox signal with a formal redox potential (E^0) of +177 mV vs. SCE and a peak separation (ΔE_p) of 33 mV in the absence of O₂, and a maximum background corrected catalytic current density (Δj_{max}) of 31.2 ± 1.1 µA cm⁻² at ca. 160 mV vs. SCE in air-equilibrated solution. An onset potential of 405 ± 5 mV vs. SCE is observed, arbitrarily obtained by comparing the CVs of the bioelectrode in the presence and absence of dioxygen¹. The attenuated current density when the potential is below 160 mV vs. SCE in **Fig. 2** reveals a O₂ supply limitation region²⁰. With PTFE capping, the CV in the absence of solution-phase O₂ exhibits slightly increased current density, retaining the same E^0 . This observation is consistent with our previous report that more redox polymer can be electrochemically addressed when an additional coating is applied²⁰. However, the ORR in the presence of solution-phase

O₂ decreased to 26.8±0.7 μA cm⁻². It seems that BOx entrapped in Os(bpy)₂PVI is not in close proximity to the O₂ carrier, *i.e.* PTFE to improve current density for ORR in this configuration.

Fig. 2. Cyclic voltammograms (CVs) of GCE/Os(bpy)₂PVI-BOx (black curve) and two-layered GCE/Os(bpy)₂PVI-BOx/PTFE (red curve) in either Ar- (solid curve) or air-equilibrated (dashed curve) 0.1 M pH 7.0 PBS; Scan rate: 5 mV s⁻¹.

PTFE was thus mixed within the redox polymer/BOx layer (**Scheme 1C**) to provide GCE/Os(bpy)₂PVI-BOx-PTFE(*n*) electrodes, where *n*=0, 2, 4 and 6, corresponds to the employed volume (in μl) of 20% PTFE water suspension (details in ESI[†]). As shown in **Fig. 3**, CVs of GCE/Os(bpy)₂PVI-BOx-PTFE(*n*) vary in terms of shape and peak currents, although all share the identical E^{0'} of +177 mV vs. SCE in the absence of solution-phase O₂. Surface coverage (Γ, nmol cm⁻²) of osmium on the electrode (eq. s1), estimated by integrating the area under the reduction peak in the absence of O₂ (**Fig. 3A-D**) is 0.20 nmol cm⁻² when *n*=0, remaining a similar level (0.18 nmol cm⁻²) for *n*=2, while seeing a decrease for *n*=4 (0.12 nmol cm⁻²) and *n*=6 (0.10 nmol cm⁻²). The monolayer coverage of Os polymer is 0.10 nmol cm⁻²²¹, indicating that the electrochemically inert PTFE submicro-rods render a proportion of the osmium redox polymer inaccessible for electrical wiring to the electrode. Moreover, with increasing *n*, the CVs in the absence of solution-phase O₂ display an overlap of the osmium redox signal with an irreversible reduction. This irreversible wave is indicative of ORR (**Fig. 3A-D**) demonstrating the PTFE can retain O₂ even though the solution has been completely degassed in a well-sealed electrochemical cell (**Fig. S2**). To further confirm the irreversible CV for *n*=6 is due to ORR, the addition of the inhibitor²² 0.2 M F- makes the CV less irreversible (data not shown) and a control electrode GCE/Os(bpy)₂PVI-PTFE(6) without BOx shows a quite reversible CV (**Fig. S3**). The observed ORR of GCE/Os(bpy)₂PVI-BOx-PTFE(6) in Ar-equilibrated solution is consistent with the observation of Jeerapan et al.¹⁵ that hydrophobic PCTFE could adsorb O₂ and provide inertial O₂ supply for Pt catalysts in an oxygen-deficit condition.

Fig. 3. CVs of mixed-type GCE/Os(bpy)₂PVI-BOx-PTFE(*n*) (*n*=0, 2, 4, 6) in either Ar-(solid curve) or air-equilibrated (dashed curve) 0.1 M pH 7.0 PBS; Scan rate: 5 mV s⁻¹.

The GCE/Os(bpy)₂PVI-BOx-PTFE(*n*) electrodes were further tested in air-equilibrated 0.1 M pH 7.0 phosphate buffer solution (PBS) (**Fig. 3E-H**). The *n*=2 cathode registers the highest ORR Δ*j*_{max} of 36.6±2.2 μA cm⁻² (**Fig. S4**), outperforming GCE/Os(bpy)₂PVI-

BOx-PTFE(0) ($31.2 \pm 1.1 \mu\text{A cm}^{-2}$) by 17% (**Fig. S4**). For comparison, coating a hydrophilic poly(acrylic acid) layer onto GCE/Os(bpy)₂PVI-BOx showed an unchanged ORR Δj_{max} due to limited O₂ supply, although the amount of Os polymer available as a mediator was increased²⁰. It can be concluded that in this configuration of PTFE submicro-rods mixed within layers on electrodes can serve as “oxygen tanks” (**Scheme 1C**). However, Δj_{max} declined to 29.3 ± 1.8 and $26.5 \pm 1.2 \mu\text{A cm}^{-2}$ for $n=4$ and 6, respectively (**Fig. 3G-H, Fig. S5**), consistent with the decreased Γ of osmium for these electrodes (**Fig. 3C-D**). The highest current density for GCE/Os(bpy)₂PVI-BOx-PTFE(2) is likely a compromise between oxygen-carrying and electrically insulating properties of PTFE, and this electrode configuration is selected for testing of operational stability of ORR current.

Operational stability is a crucial parameter for feasibility of ORR cathodes¹. This was examined by measuring current on application of a constant potential of 0.1 V vs. SCE in air-equilibrated PBS for GCE/Os(bpy)₂PVI-BOx and GCE/Os(bpy)₂PVI-BOx-PTFE(2) electrodes (**Fig. 4**). The GCE/Os(bpy)₂PVI-BOx ORR current decreases within an initial 7 h, after which negligible current density is registered. Such a dramatic drop is mainly attributed to the detachment of redox polymer and enzyme from the electrode¹⁷. In a striking comparison, the GCE/Os(bpy)₂PVI-BOx-PTFE(2) electrodes shows a first phase of ORR current stabilisation over 2 h with ORR current declining by 16%, but then the ORR current remains constant for another 14 h. Recently, Slack et al. showed that polyvinylidene fluoride (PVDF) as a binder component improved the durability of Pt/C cathodes due to the hydrophobic PVDF stabilized the carbon support for Pt and electrode structure²³. In our case, it is likely that PTFE binds well to the hydrophobic GCE, resulting in lower redox polymer leakage and enzyme from the electrode.

In conclusion, commercial PTFE submicro-rods have been combined with redox polymer and BOx to improve ORR cathode performance. A bilayer configuration shows no improvement of ORR performance, because PTFE cannot interact with BOx in such a configuration. In contrast, mixing an amount of PTFE with redox polymer and BOx exhibits both enhanced ORR current density and operational stability. The concept demonstrates that employing PTFE as “oxygen tanks” in a submicro-level could be applied in high-performance bio-/cathode development, even finding applications in anaerobic conditions. Alteration to the size and shape of PTFE, and to the applied potential waveform, to introduce switching on and off ORR, is expected to further improve the performance of such a mixed-type ORR cathodes.

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Fig. 4. Operational stability of GCE/Os(bpy)₂PVI-BOx (black curve) and GCE/Os(bpy)₂PVI-BOx-PTFE(2) (red curve) in air-equilibrated 0.1 M pH 7.0 PBS; applied constant potential: 0.1 V vs. SCE.

Conflicts of interest

There are no conflicts to declare.

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