Electrochemical transistors with ionic liquids for enzymatic sensing

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Introduction:

• Point-of-care (POC) glucose biosensors play an important role in the management of blood sugar levels in patients with diabetes.

• One of the most commonly used enzymes in glucose biosensors is Glucose Oxidase (GOx).

• Recent developments in the field of organic electronics have made available a variety of devices that bring unique capabilities at the interface with biological macromolecules[1].

• Organic electrochemical transistors (OECTs) have been developed for a variety of biosensing applications, including the detection of ions, metabolites and antibodies[2].

• A polymer that is commonly used in OECTs is poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT : PSS).

• Ionic liquids (ILs) have evolved as a new type of solvent for biocatalysis, mainly due to their unique and tunable physical properties.[3]

• Enzymes have been found to retain their selectivity, stability and in some cases even enhance their catalytic activity in an IL medium, though this last point is still a matter of debate[4].

Aim:

To develop an enzymatic sensor based on an OECT that uses an IL as an integral part of its structure. The strategy we follow involves patterning the RTIL over the active area of the OECT, and using it as a reservoir for the enzyme and the mediator.

Experimental:

• Important properties of the electrolyte for this device must include wetting the PEDOT : PSS film.

• This allows the enzyme and the mediator to be patterned over the active area of the device.

• The IL should be miscible with the aqueous phase (PBS).

• Triisobutyl(methyl)phosphonium Tosylate ([$P_{1,4,4,4}$][Tos]) (Fig 1) due to the hydrophilic nature of the cation / anion.

• [$P_{1,4,4,4}$][Tos] was purified as previously described in the literature[5].

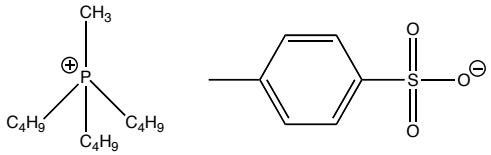

Fig 1: [$P_{1,4,4,4}$][Tos] Ionic Liquid used in this study. (provided by Cytec Canada Inc. Ontario, Canada)

• Fig 2 shows the fabrication process of the OECT

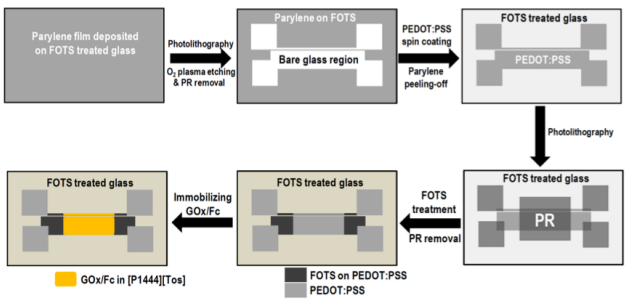

Fig 2: OECT fabrication.

Results & Discussion:

• Fig 3a shows the transient response of the drain current of an OECT upon application of a gate voltage of 0.4 V and duration of 3 min. The drain voltage was -0.2 V.

• Current modulation (represented as the dimensionless quantity ΔI/I) of the OECT as a function of glucose concentration. Inset shows the concept of device operation, and the arrows indicate the dissolution of the RTIL carrying the enzyme and the mediator into the analyte solution.

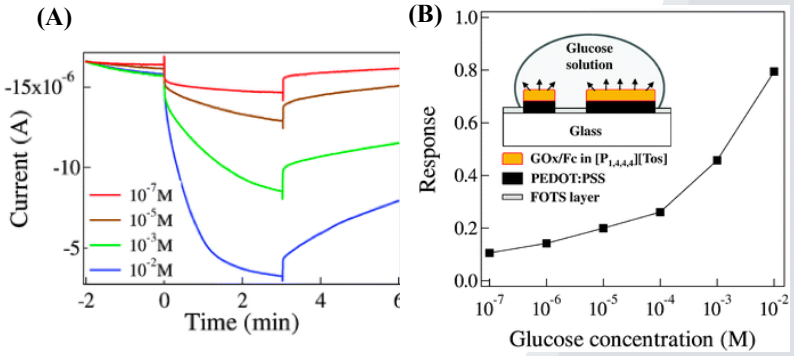

Fig 3: (A) Transient response time of the drain current of the fabricated OECT with integrated IL as electrolyte. (B) Current modulation (represented as the dimensionless quantity ΔI/I) of the OECT as a function of glucose concentration.

• The data show the characteristic decrease of drain current upon gating which has been understood on the basis of the reactions shown in Fig. 4.

• As glucose in the solution is oxidised, the enzyme (GOx) itself is reduced, and cycles back with the help of the Fc/ferricenium ion (Fc+) couple, which shuttles electrons to the gate electrode (Fig. 4a).

• For example, for 10^{-2} M of glucose, this cascade of reactions causes a current of $8x10^{-8}$ A to flow to the gate electrode. At the same time, cations from the solution (M+) enter the PEDOT : PSS channel and dedope it (Fig. 4b).

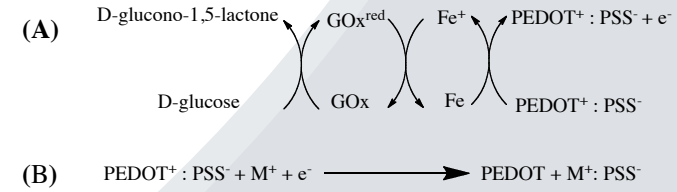

Fig 4: Reactions at the gate electrode (a) and at the channel (b) of the OECT.

Conclusions:

• Successful integration of an OECT with an IL as electrolyte.

• The ionic liquid was confined on the surface of the transistor using a photolithographically patterned hydrophobic monolayer

• The enzyme was in a dispersed state in the ionic liquid, which may prove to be a good strategy for improving long-term storage.

• Using the glucose/ glucose oxidase pair as a model, we demonstrated analyte detection in the 10^{-7} to 10^{-2} M concentration range.

References

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