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).
- Ionic liquids (ILs) have evolved as a new type of solvent for biocatalysis, mainly due to their unique and tunable physical properties.[1]
- Amperometric biosensors employing IL's have been reported previously, for example, ([C_4mIm][BF_4]) has been used as a mediator in a electrochemical H_2O_2 biosensor[2].
- This work investigates colorimetric and electrochemical methods of glucose detection by Combining the enzyme's specificity, with the unique characteristics of IL's and either a *chromogen* (o-Dianisidine) or electrochemical *mediator* (ferrocene) to enhance the detection.
- This interest is driven by the need to find molecular environments in which enzymes are highly stabilized while retaining redox activity.

Experimental:

- Ionic liquids used in this study include [C_2mIm][$EtSO_4$], [$P_{6,6,6,14}$][Cl], [$P_{6,6,6,14}$][dca] and [$P_{6,6,6,14}$][NTf_2] (Fig 1).

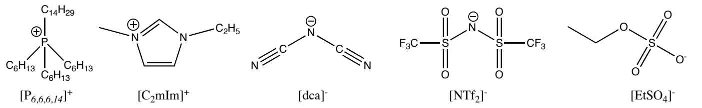

Fig 1: Cations / anions used in this study.

Colorimetric:

- The mechanism of the GOx / peroxidase reaction is shown in Fig 2 for colorimetric analysis. Glucose is quantified via the indirect oxidation of o-Dianisidine.

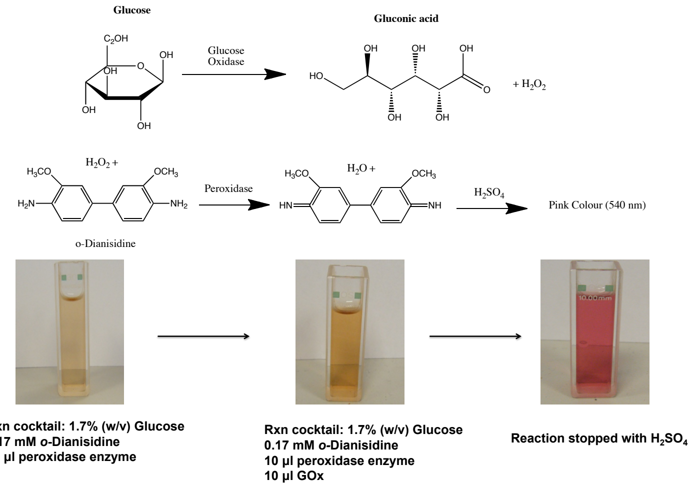

Fig 2: Glucose quantification measured using colorimetric analysis.

Electrochemical:

- Counter & working electrode consisted of Carbon Cloth- Graphitized Spun Yarn Carbon Fabrics
- 500 µm threads consisting of a bundle of 10 µm fibres.
- Allows for flexible substrates.
- Potentials were against a Ag/AgCl reference electrode – 500 µm silver wire chloridised in $FeCl_3$.
- Single threads were soaked in a IL / Ferrocene / GOx enzyme solution
- The electrochemical mechanism for glucose detection in a Ferrocene mediated system[3]:

$$\text{GOx-FAD}^{+} + \text{Glucose} \rightarrow \text{GOx-FADH}_2 + \text{Gluconolactone}$$
$$2\text{Fe}^{+3} + \text{GOx-FADH}_2 \rightarrow 2\text{Fe}^{+2} + \text{GOx-FAD}^{+}$$
$$2\text{Fe}^{+2} \rightarrow 2\text{Fe}^{+3} + 2\text{e}^{-} \qquad \text{@ electrode surface}$$

Results & Discussion:

Colorimetric:

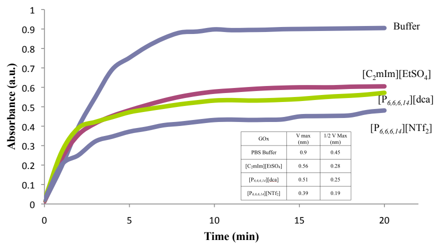

Fig 3: **Colorimetric assay for GOx in different ILs at 0.55 M glucose .**

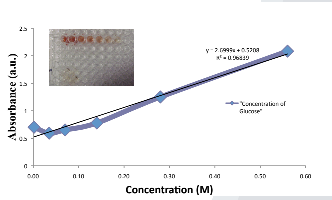

Fig 4: **Standard curve of GOx assay with [C_2mIm][$EtSO_4$] & varying glucose concentrations.**

- [C_2mIm][$EtSO_4$] showed favourable results for colorimetric analysis (Fig 3).
- Varying concentrations of glucose in [C_2mIm][$EtSO_4$] resulted in a linear standard curve (Fig 4).

Electrochemical:

- SEM image (Fig 5) shows excellent coverage of the threads resulting in a large working surface area. Using the Anson equation, the calculated working area was approx 0.138 cm^2.
- Due to the hydrophobic nature of the cloth, [$P_{6,6,6,14}$][dca] was chosen as the electrolyte.
- Significant response shown at 7.5 mM glucose addition (Fig 6).

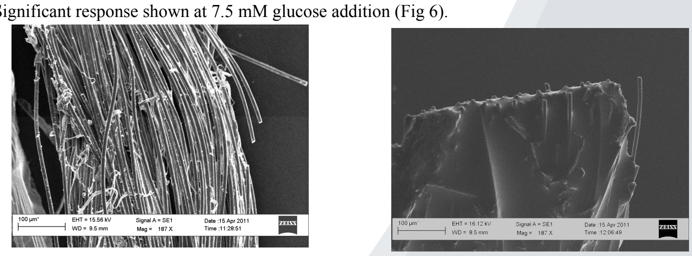

Fig 5: SEM images of carbon cloth & carbon cloth soaked in **[$P_{6,6,6,14}$][dca] / Ferrocene / Gox.**

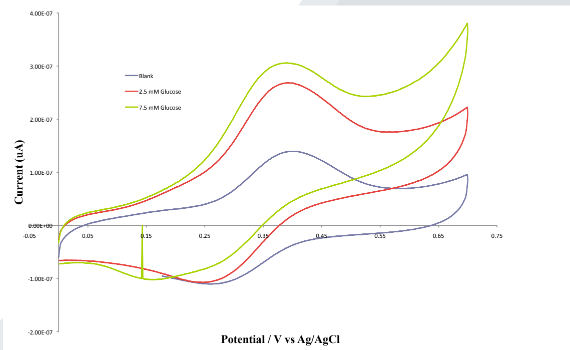

Fig 6: CV of Glucose additions to [$P_{6,6,6,14}$][dca]/Ferrocene/Gox on carbon cloth. Scan rate 0.01 V/S

Conclusions:

- [C_2mIm][$EtSO_4$] showed favourable results for colorimetric analysis (Fig 3).
- Carbon cloth shows potential as a flexible working electrode.
- [$P_{6,6,6,14}$][dca] as an electrolyte in the glucose system shows favourable limit of detection
- A flexible, wearable one shot sensor maybe produced using IL formulations

References

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