Inks and Printing Methods for Biosensors
Outline of Presentation

• Manufacturing flow diagram
• Substrate materials
• Transducers - what role do they play
• Materials used in printed biosensors
• Application techniques – screen printing and others
Printed Transducer

- **Definition** – power transforming device for which the input and output are of different kinds of energy

- In an electrochemical biosensor chemical energy is transformed into electrical energy
What's So Special about Materials for Electrochemical Transducers

- Electrochemistry is a surface technique - for electrochemical reactions to occur the surface of electrode materials must be clean and have active materials available.

- All material systems must have active material at the surface i.e. not coated with polymers

- Inks are formulated to allow this to happen but screen printing and other physical properties are sacrificed to achieve this
Batteries and biosensors

• A demonstration electrochemical cell setup resembling the **Daniell cell**. The two half-cells are linked by a salt bridge carrying ions between them. Electrons flow in the external circuit.
Substrates Used in Base Transducers

- Polyester
- PVC
- Polycarbonate
- Polystyrene
- Alumina
PET Polyester

- Is the most commonly used substrate thickness of substrate from 90-500 microns
- Most common thickness 350 to 500 microns
- Highest cure temp how long?
- Normal 120 to 130 °C
Major Ink Systems

- Particulate
- Organo-Metallic
- Precious Metal
- Base Metal
- Ceramic
- Carbon
- Polymer
- Dielectrics
Major Application Methods

- Screen Printing
- Ink Jet
- Syringe
- Spraying
- Other printing methods (not yet)
Screen – Printed Materials Commonly Used in Disposable Biosensors

- Carbon – graphite mixes
- Silver conductors
- Silver/silver chloride reference electrode materials
- Insulators / Dielectrics
- Adhesives
## Differences between functional and graphic inks

<table>
<thead>
<tr>
<th>Graphic ink</th>
<th>Functional carbon ink</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Polymer 15-25 pbw</td>
<td>• Polymer 5-09 pbw</td>
</tr>
<tr>
<td>• Filler 35-10 pbw</td>
<td>• Filler 38-42 pbw</td>
</tr>
<tr>
<td>• Solvent 50-65 pbw</td>
<td>• Solvent 57-49 pbw</td>
</tr>
</tbody>
</table>

**Why manufacturers make poor printing inks**
Major Constituents of Carbon Inks

- Functional phase: 38 to 42 parts by weight
- Polymer carrying system: 4 to 9 parts by weights
- Solvents usually 3 different: 11 to 58 parts by weight

50 microns wet

25 microns cured
Materials and their roles

• Carbon black and synthetic graphite
  Role: Carry the current

• Polymers
  Role: Adhere material to substrate

• Solvents
  Role: Lower viscosity for application method
Major constituents of carbon inks and their roles

- Base polymer system consists of a thermoplastic polymer and solvents; to adhere to base substrate
- Functional filler carbon black and graphite; to conduct electrons and interface with ions
- Mixed solvent system; to allow printing and drying without disrupting print film
Vehicles (polymers + solvents)

- Almost all polymers used are thermoplastic

- 2 or 3 different solvents are used of differing evaporation rates

- Dispersed together to form the base system

- Thermoset polymers are used in conjunction with sensors needing membranes
Solvents and their role

- Viscosity modifier for polymer vehicle
- Controls viscosity of printing ink
- Allows drying without cracking film of electrode
Plot of Viscosity

<table>
<thead>
<tr>
<th>γ [1/s]</th>
<th>η [Pas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>9.457</td>
</tr>
<tr>
<td>100.0</td>
<td>7.045</td>
</tr>
<tr>
<td>200.0</td>
<td>4.863</td>
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<tr>
<td>230.0</td>
<td>4.536</td>
</tr>
<tr>
<td>300.0</td>
<td>3.942</td>
</tr>
<tr>
<td>400.0</td>
<td>3.379</td>
</tr>
</tbody>
</table>

- Low shear at beginning of print stroke
- Higher shear during print stroke, reduced viscosity
- Newtonian viscosity
Ink dispersion methods

- Dispersing particulate ink is a 2 stage process
  - 1\textsuperscript{st} low shear mixing
  - 2\textsuperscript{nd} high shear mixing
- Mixing technology similar to cake baking
Dispersion
a 2 stage process

Planetary mixing low shear process

3 roll mill high shear process
Testing functional systems

- The vast majority of commercial systems are based on measuring current.
- As ink manufacturers we are unaware of customers' individual needs.
Cyclic voltammetry

- **Definition:** a method for determining the kinetics of electrode processes. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.
Cyclic Voltammetry

Method employed to determine the oxidation potential of Carbon/Graphite pastes

Print Electrodes Design No. BE2031028

Buffered Ferricyanide Solution – 0.5mM Potassium ferricyanide in 0.1M buffer and KCl, pH7.5

Cyclic voltammetry performed using ferricyanide solution from +0.8V to -0.4V to +0.8V at 10mV/s

Interested in the position of the oxidation peak and the CV% of the triplicate tests
Cyclic Voltammogram

Depletion of material at electrode surface

Max. diffusion

I (µA)

E (mV)
Diffusion layer at macroelectrode

- Diffusion layer is the concentration gradient at the electrode surface until it reaches the bulk concentration.
- The size of the diffusion layer depends on the mass transfer coefficient and is time related.
Electrochemical cell and the role of each electrode

A typical electrochemical cell is formed of three electrodes:

- **Working electrode**: the electrode at which the electrochemical reaction takes place. It is usually made of carbon/graphite, mediated carbon, gold, platinum etc.
Counter (auxiliary) electrode

- It is collecting and transferring the current generated at the working electrode. It has to be highly conductive and chemically inactive and has to be in the close proximity of the working electrode; material used preferable platinum but carbon and silver are good options.
Reference electrode

- It has to provide a good reference potential for the working electrode.
- Examples of reference electrodes: Ag/AgCl, saturated calomel, hydrogen electrode (the 0V reference electrode), carbon as pseudo-reference electrode.
- When using carbon pseudo-reference electrodes is important to ensure the potential is established through a different way. In the case of the glucose biosensor the potential is established by using a high concentration of Fe3+/Fe2+ mediator.
Electrochemical cell and the role of each electrode

- The potential is applied between the reference and the working electrode hence the importance of having a good reference electrode.

- The current is measured between the working and the counter electrodes.
Electrochemical cell and the role of each electrode

- When the measured currents are relatively high (nA or rather µA) the counter and the reference electrodes can be combined as one electrode. This is the case for screen printed electrodes with Ag/AgCl or carbon combined reference and counter electrode.

Three electrode system

Two electrode system
Enzyme based inks

- Some commercial manufacturers print a discrete enzyme layer
- This only for GOX based biosensors
- Others use liquid deposition equipment for bio-cocktail systems
Enzyme solutions

• Stabilised enzyme solutions are commercially available

• Most manufacturers customise these systems to meet their own requirements

• Other stabilised enzyme solutions are available
Materials Available for Special Applications

- Cross-linked systems suitable for membranes (polar or strong solvents) and FIA applications
- High temperature systems available for ceramic substrates (alumina)
- Gold, Platinum, Palladium, Rhodium in both polymeric and high temperature systems
- Other metals such as Nickel and Copper if needed
Why is Screen-Printing Popular

- Cheap for small volumes - less than 1 billion sensors per year
- Film thickness can be high (>40µm)
- Other printing techniques give lower weights of deposit
What About Other Methods?

- Flexographic and Gravure printing lower weight of deposit
- Web based printing for volumes over 1 billion and expensive set-up costs
- Rotary screen printing needs different viscosity inks
- Liquid dispensing needed for enzymes other than glucose oxidase
- Dot on demand ink jet pico litre drop sizes and production cycle time issues will be used for smaller structures
Sensor Design and Application Techniques

- The limit of traditional screen printing was 70 micron lines and spaces
- The new limit is 20 micron lines and 100 micron spaces
- With new inks this is the new limit of the screen printing technique
- A new screen is needed for each printed layer
- Art work needs to be generated for each screen
Screen Printing

**Printing speed:**
60 - 1500 sheets per hour
The Screen Printing Process

Fig 1 The basic screen print process
Normal printing 2/3 of screen area can be used.

For high definition ½ of screen area can be used.
Curing of Printed Electrodes

- For a few prototypes simple oven curing is acceptable - temperature ranges will depend upon the substrate used for most grades of polyester 60-110 deg C can be used.

- For production quantities a IR belt furnace is often used; the temperature of drying can be reduced if air flow is increased

- Some manufactures use rotary wicket driers in an attempt to save production space
Electrode Polymer Curing Unit
Dek248 Production Printer
Screen printing & manufacturing volumes

• Low volume production (3.5 Million per month)
• High Volume (100 million per month)
• Volumes made by flat bed printing
• Higher volumes use web printing
• Higher accuracy use optical printing
Rotary Screen Printing
Sensitivity and Limits of Detection

• Screen printed electrodes can measure analytes in the nanomolar range.

• Many environmental applications require low ppb limits of detection.
Finer lines and pitch

• The limits of screen printing in production is 100 microns track and gap
• Many research projects are being carried out to print finer details
• GEM are working to develop new techniques in this area
Print Limitations

300SDS 40µm

400UT 40µm

V330 40µm

C2090903R3 76% Pt
Flexography

TYPICAL PRINT STATION OF A FLEXO PRESS
Recap on printing speeds

- Flat bed printing 50 to 1500 sheets per hour
- Web based systems 9 to 15 metres per min
- Flexo printing 40 to 120 metres per min
- Some history early 1990’s flat bed production
- 2000 web based systems
Technology and production

- Practical: let's assume a 10 second production period.
- Flat bed 200 prints per hour - half a sheet of electrodes printed
- Web based systems 10 metres/min - 1.7 metres of electrodes printed
- Flexo 60 metres/min – 10 metres of electrodes printed
Application Methods for Biomaterials

- The only enzyme system commonly printed is Glucose Oxidase
- Many enzyme systems cannot be applied with ink jet systems
- The more sensitive systems are applied using liquid dispensing methods
Conclusions

• Screen-printing is the most commonly used application method for base transducers
• Screen-printing can be used with enzymes
• A variety of application techniques can be used with bio–systems
• The limit for small structures in the future will be ? lines and spaces
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