Ionogel Materials for Fluid Control and Sensing in Microfluidic Devices

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Dublin City University
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National Centre for Sensor Research

- OVER 260 RESEARCHERS AND SUPPORT STAFF
- 23 AFFILIATED FACULTY
- INVESTMENTS AND INCOME SINCE 1999 NOW APPROACHING €100 MILLION
- 1500 m² WELL-EQUIPPED SPECIALIST LAB SPACE AND OFFICE
CLARITY – SFI CSET

Vision: Sensing Mind, Body & Place

- 5-YEAR, €16.4 MILLION RESEARCH PROGRAM TO DEVELOP NEXT GENERATION SENSOR WEB TECHNOLOGIES WITH SIGNIFICANT ENVIRONMENTAL FOCUS

- BRINGS TOGETHER FUNDAMENTAL MATERIALS SCIENCE, FUNCTIONAL POLYMERS, DEVICE PROTOTYPING, ENERGY MANAGEMENT, ADAPTIVE MIDDLEWARE, WEARABLE SENSORS, DISTRIBUTED ENVIRONMENTAL MONITORING ....
Sensor Hierarchy

- PHYSICAL TRANSDUCERS – THE GOOD GUYS; LOW COST, RELIABLE, LOW POWER DEMAND, LONG LIFE-TIME
  - THERMISTORS (TEMPERATURE), MOVEMENT, LOCATION, POWER, LIGHT LEVEL, CONDUCTIVITY, FLOW, SOUND/AUDIO, …

- CHEMICAL SENSORS – MORE COMPLICATED, MISBEHAVE, NEED REGULAR CALIBRATION, MUCH MORE COSTLY TO IMPLEMENT
  - ELECTROCHEMICAL, OPTICAL, .. FOR METAL IONS, PH, ORGANICS…

- BIOSENSORS – THE WORST OF ALL, VERY DIFFICULT TO WORK WITH, DIE QUICKLY, SINGLE SHOT (DISPOSABLE) MODE
  - DUE TO THE DELICATE NATURE OF ENZYMES, ANTIBODIES….
BUT CAN WE USE THESE SENSORS IN CONTINUOUS DIRECT CONTACT WITH REAL SAMPLES TO PROVIDE LOW COST, AUTONOMOUS SENSING PLATFORMS...
Fundamental Problem: Sensor surface will change with time!

SURFACES SUSCEPTIBLE TO BIOFOULING: THE SENSOR SAMPLES THE BIOFILM LAYER, NOT THE BULK SOLUTION!

=> DRIFT, LOSS OF SENSITIVITY/LOD/SELECTIVITY => REGULAR CALIBRATION (LIQUID HANDLING) => HIGH COST OF OWNERSHIP
Direct Sensing vs. Reagent Based LOAC

DIRECT SENSING

OUTSIDE WORLD

SENSOR

SAMPLE

SIGNAL

MOLECULAR INTERACTIONS

LOAC ANALYSER

SAMPLE, REAGENTS

SOURCE

SAMPLE, STANDARDS

WASTE

REACTION MANIFOLD

DETECTOR

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SAMPLE

BLANK

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ITY
MANY PEOPLE, MYSELF INCLUDED, EXPECTED THAT THE ABILITY TO MANIPULATE FLUID STREAMS, IN MICROCHANNELS, EASILY, WOULD RESULT IN A PROLIFERATION OF COMMERCIAL LOAC SYSTEMS, AND THAT WE WOULD SEE APPLICATIONS OF THESE DEVICES PROLIFERATING THROUGHOUT SCIENCE. IN FACT, IT HAS NOT (YET) HAPPENED.

EDITORIAL ‘SOLVING PROBLEMS’, GEORGE WHITESIDES
LAB CHIP 10 (2010) 2317-2318
Use of microfluidics for the solution of problems?

Problem ↔ Microfluidic Technology

Better than existing technology

Market

Development!!!
Achieving Scale-up

1. EVOLUTIONARY DEVELOPMENT, COST DRIVEN DOWN, RELIABLE, IMPROVED SCALABILITY

2. REVOLUTIONARY MATERIALS BREAKTHROUGHS; HIDDEN COMPLEXITY, BIOMIMETIC PLATFORMS, ALL FLUID HANDLING INTEGRATED ON CHIP, INDEFINITELY SELF-SUSTAINING

CURRENT PLATFORMS

MASSIVELY SCALED DEPLOYMENTS OF THE FUTURE
Disadvantage of Microfluidics

NEW GENERATION OF MICROFLUIDIC DEVICES

↓

ADVANCES IN FUNDAMENTAL MATERIAL SCIENCE

$CO_2$ cylinder

Photoswitchable Materials

- Optically actuate between two distinct isomers
- Control physico-chemical properties of system
- Non-contact spatial control of actuation
Multiple Personalities!

SOLVATOCHROMIC

Metal ions, proton, protein and DNA recognition site

THERMOCHROMIC

Thermal relaxation dependent on all processes!
Photo-responsive polymer

PROTONATED ISOMER INCORPORATED INTO CROSS LINKED THERMORESPONSIVE HYDROGEL

IRRADIATION OF BLUE LIGHT RESULTS IN CONTRACTION OF HYDROGEL

EXCELLENT SPATIAL RESOLUTION

TECHNICAL ISSUES INCLUDE EVAPORATION OF WATER FROM HYDROGEL
Ionic Liquids- photoresponsive liquids

CONSIST SOLELY OF IONS AND LIQUIDUS AT RT
NEGLIGIBLE VAPOUR PRESSURE, NON-FLAMMABLE, THERMALLY STABLE AT HIGH TEMPERATURES
DESIGNER SOLVENTS (VISCOSITY, POLARITY, ACIDIC-BASIC, ELECTROCHEMICAL, ...)
ABILITY TO TUNE ION COMPOSITION
APPLICATIONS IN CATALYSIS, SEPARATIONS, POLYMERIZATIONS (IONIC LIQUIDS IN GELS, SOLID STATE ELECTROLYTES)

THE NUMBER OF PAPERS PUBLISHED IN 1995 WAS APPROXIMATELY 20 AND ROSE TO 2,500 IN 2006.

COMBINATION OF IONOGEELS AND PHOTO-RESPONSIVE MATERIALS OFFERS MANY ADVANTAGES!!!!

Preparation of photo-responsive ionogel

HYDROXYL-BENZOSPIROPYRAN \( \rightarrow \) ACRYL ESTER BENZOSPIROPYRAN

ACRYLOL CHLORIDE

1) Ionic Liquid
2) 365 nm Irradiation 10 mins
3) 1mM HCl

IONOGEL

BYRNE ET AL., BIOSENS & BIOELECTRON, 26, 2010, 1392-1398
PHOTO-POLYMERISATION TAKES PLACE IN IONIC LIQUID MATRIX
IONOGELS HAVE DIFFERENT CHEMICAL AND PHOTO-PHYSICAL PROPERTIES DUE TO IONS WITHIN THE GEL.


SPECTROSCOPIC ANALYSIS
RATE CONSTANT = 2.5 x10^-2s^-1
Photo-responsive ionogel properties
Physical characterisation of ionogel

ALL MEASUREMENTS AT 25 °C

CORRELATION BETWEEN STIFFNESS AND ACTUATION BEHAVIOUR

Table 1  Axial stiffness, ultimate tensile strength (UTS) and elongation at break values for the ionogels

<table>
<thead>
<tr>
<th>Ionogel</th>
<th>Axial stiffness/N mm⁻¹</th>
<th>UTS/MPa</th>
<th>Elongation at break (%)</th>
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<tr>
<td>[dbsa]⁻</td>
<td>0.1713</td>
<td>0.12</td>
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<tr>
<td>No I.L.</td>
<td>0.0493</td>
<td>0.08</td>
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<td>[dca]⁻</td>
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<td>[NTF₂]⁻</td>
<td>2.9340</td>
<td>0.22</td>
<td>68.210</td>
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</table>
Photo-responsive valve: Chip fabrication

Multiple valves on one chip, using one actuation source!

Magnetic control of hydrophobic liquids

Hydrophobic Ionic liquids (Phosphonium and Imidazolium based magnetic ionic liquids)
Prepared by salt metathesis with paramagnetic anions (Fe, Gd, Co, Mg)

- Non invasive control of \([P_{6,6,6,14}]\text{[FeCl}_4]\) ionic liquid
- Disruption of laminar flow in micro fluidic channels
- Liquid tube stabilisation

50ul of \([P_{6,6,6,14}]\text{[FeCl}_4]\) in water
Chemical Sensor

Stable after 20 cycles

BASE

ACID

Chemical Sensor

- Cheap
- Easy to fabricate
- No chemical modification
- No leaching

Universal
Reusable
Long term duration
Mass production

OH $\rightleftharpoons$ H$^+$

pH Meter (reference)

Barcode

pH: 1

pH: 7

pH: 14
Introduction

SWEAT, WHY IS IMPORTANT?

Sweat is naturally generated during exercise.

Monitoring its contents provides very rich information about the physiological condition of the individual.

Rehydration and re-mineralisation

Improve performance and general health

Sweat analysis: identify pathological disorders
* cystic fibrosis
* information on dehydration
• changes in the concentration of biomolecules and ions. hyponatremia (low sodium concentration)

*Common hereditary disease which affects the entire body, causing progressive disability and often early death.
Introduction

PHYSIOLOGICAL SENSORS

Breath rate, heart rate, activity, posture, skin temperature…

LIFESHIRT®

TRAINTRAK™

NIKE-APPLE IPOD SPORTS KIT
Introduction

CHEMICAL SENSORS

NASA: WEARABLE SENSOR PATCHES

GLUCOWATCH

SWEAT COLLECTION PATCHES

PharmChek Sweat Patch
Introduction

Current Ways of Sweat Collection and analysis

Introduction

PROBLEMS TO OVERCOME WITH CHEMICAL SENSOR?

SAMPLE GENERATION

COLLECTION

DELIVERY

SENSOR CALIBRATION

WEARABILITY

SAFETY ISSUES

SWEAT RATE AND FLUID LOSSES VARY FOR INDIVIDUALS AND ARE GENERALLY DEPENDENT ON BODY SIZE, GENDER, EXERCISE INTENSITY, ENVIRONMENTAL CONDITIONS AND INDIVIDUAL METABOLISM.
Introduction

WHAT DO WE NEED????

DEVICE:
WEARABLE
ROBUST
FLEXIBLE / ADAPTABLE
REUSABLE/ DISPOSABLE  CHEAP
CONTINUOUS REAL TIME ANALYSIS  IMMEDIATE FEEDBACK

MICRODEVICES!!
Introduction

DETECTION:

NOT INVASIVE

WIRELESS

FREEDOM FROM ELECTRICAL NOISE

MINIATURIZATION

NOT PHYSICAL CONTACT

FLEXIBILITY IN INTERROGATION APPROACHES
(HUMAN EYE, LED-SENSORS, CAMERAS, SPECTROMETERS, …)
Ionogel pH sensor

DOPE THE IONOGE WITH A pH-DYE

Sweat pH: 4.5-7.5

1- METHYL RED  4.4 - 6.2
2- BROMOCRESOL GREEN  3.8 - 5.4
3- BROMOCRESOL PURPLE  5.2 - 6.8
4- BROMOTHYMOL BLUE  6.0 - 7.6

DYE DO NOT LEACH OUT

DIGITAL CAMERA PHOTO RGB-MATLAB

Barcode & Micro-fluidic

- pH sensor ionogels
- Colour reference (RGB)
- Channels
- Absorbent
Characterisation

MICRO-FLUIDIC SYSTEM PERFORMANCE

$4.6 \pm 0.2 \ \mu L \ min^{-1}$

LOADING CAPACITY: $156 \pm 3 \ \mu L$

LIFE-TIME: 34 MINUTES
Results

Colour profile of each of the indicators at different pH’s (pH range: 1-14)

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<th>4</th>
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<th>5.5</th>
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<td>3</td>
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<td>12</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

Back of a trainer with a chip (1) and barcode (2) systems (activated at pH 2)
RESULTS: camera pictures and RGB colour analysis using a reference.

**Activation pH**
Results

Sweat pH determination using the barcode in an athlete during a 50 min training period

![Sweat pH measurement in an athlete](image)

Conclusions

• MICROFLUIDICS HAS ACHIEVED MUCH IN TERMS OF DELIVERING A BASIC UNDERSTANDING OF FLUID HANDLING AND ANALYTICAL MEASUREMENTS IN MICRO/NANO-CHANNELS.

• THE NEXT PHASE HAS TO DELIVER FULLY INTEGRATED AND FUNCTIONING ‘MICRO-TOTAL ANALYSIS SYSTEMS’ THAT CAN PROVIDE SOLUTIONS WITH REAL SOCIO-ECONOMIC IMPACT.

• VITAL TO COMBINE STRONG APPLIED EFFORT TO PRODUCE NEXT GENERATION PLATFORMS & PROTOTYPES (EVOLUTIONARY ADVANCES) WITH FUNDAMENTAL BREAKTHROUGHS IN MATERIALS SCIENCE (REVOLUTIONARY ADVANCES).
Thanks to.....
QUESTIONS?