Agenda

- Motivation and application opportunities for printed and hybrid functional solutions
- Facilities
- Examples
  - Printed transistors
  - Hybrid solution on paper (Case ROPAS)
  - Paper based diagnostic platform (e.g. Case Cyanodec)
  - Printed biobattery (Case Cosmetic patch)
Motivation for R2R Printed & Hybrid Functionalities

- Form factor & new functionality
  - Flexibility
  - Wide area

→ New functions to products
→ Basis for novel products

- Cost effective production
  - Low material use (per unit)
  - High volume, rapid production

- Starting largely from niche applications, a basis for disruptive innovations
Application areas for wearable, stretchable and disposable electronics and diagnostics

- Skincare
- Sports & Well-being
- Elderly care
- Smart packaging
- Environmental diagnostics
Application areas for printed and hybrid functionalities on large-area surfaces

- Painted walls
- Media surfaces
- Textiles
- Furnitures
- Floors
- Windows
World class research facility

**Concept development in Lab-scale**
- Ink jet printing environment
- Laboratory scale printing (flexo, screen, reverse offset, gravure)
- Chemical and biochemical laboratory facilities
- Measurement & characterisation

**Upscaling in pilot factory**
- NICO – inert roll-to-roll pilot line
- PICO – in-air roll-to-roll pilot line
- TESLA – functional testing
- ROKO – in-air roll-to-roll pilot line
- ENGEL - Injection moulding
- EVO - R2R assembly and bonding

**Best Technical Development Manufacturing Award**

**Proof-of-concept**
- MAXI – In-air roll-to-roll pilot line

**Proof-of-manufacturability**
Examples of printed electronic systems

Organic photovoltaics: electrical balance, people amount counter, presence sensor, energy harvesting tree, dollhouse, overmoulded OPV, …

Printed OLEDs: signage and displays, over-moulded OLED, …

Printed organic transistors

Replication: R2R imprinted diffractive optics, microfluidics, back-/front light, light redirection, …
Examples of printed and hybrid solutions

- Printed fluidic channels on paper, Paper-based test for consumers to detect e.g. toxic cyanobacteria
- Intelligent swimming paddle (Trainesense), Flexible wireless platform for wearable applications, Communicating envelope for insured letters with embedded electronics on paper, Printed sensor arrays
- Intelligent packaging: Visible labels for package integrity and anti-tampering, Direct digital marking of consumer products, Package integrated smart phone readable sensor for food product quality
- Printed biobattery improving effect of cosmetics, cardboard integrated device for iontophoretic skin treatment
Printed transistors

*Organic materials, metal oxides*

Ari Alastalo, Henrik Sandberg et al.
Printed transistors

- VTT is developing printed TFTs based on organic materials, oxides and CNTs.
- Organic materials have reached highest maturity and have been demonstrated on R2R
- Oxide materials have the highest performance but need special curing techniques for low-temperature annealing
- Applications targeted include sensor arrays, sensor tags and logic of functional cards.
Organic materials – sheet process

Ring oscillator

Ring oscillator output

Printed sensor and switching transistor arrays on flexible substrate*

Logic circuits

Organic materials – R2R process 1 - self-alignment for bottom gate

Metal gate electrode and wiring:
Resist printing (MAXI, flexo) + Ag Evaporation (EVA) + Lift-off (ROKO): Gate width 20 μm

Organic dielectric printing:
1st and 2nd layer (ROKO, reverse gravure)

Metal source & drain electrode formation:
Resist printing (ROKO, flexo) + Backside exposure (ROKO) + Development (ROKO) + Resist printing (MAXI, flexo) + Evaporation (EVA) + Lift-off (ROKO)

Organic semiconductor printing:
1st and 2nd layer (ROKO, reverse gravure) + lamination (ROKO)

Organic materials – R2R process 2 - Low number of processing steps for top gate

**Metal source & drain electrode:**
Ag Evaporation (EVA) or readily metallized substrate
Gel etch printing (MAXI/ROKO, screen / gravure)
→ TFT channel width 100 µm (30 µm lab process)

**Organic semiconductor and dielectric direct printing:**
1) Semiconductor solution (MAXI, gravure)
2) Dielectric solution (MAXI, gravure)

**Metal Gate electrode formation:**
Direct printing of metal particulate ink
- Ag (MAXI, screen/flexo)
- InkJet printing
Optionally: Printed organic gate or metal shadow mask evaporation

- M. Vilkman et al., "Fully roll-to-roll processed organic top gate transistors using a printable etchant for bottom electrode patterning" Organic electronics, Volume 20, May 2015, Pages 8–14
Oxide materials – sheet process with UV

- Indium nitrate (In(NO₃)₃·xH₂O, 99.9%) and Zn nitrate precursor in 2-methoxyethanol (2-ME, 99.8%) solvent
- Si, glass or PI substrate
- Bottom-gate-top-contact TFT structure
- Evaporation of Al gate electrodes using a shadow metal mask (glass / PI).
- ALD growth at 300 °C of 90 nm of Al₂O₃ insulator to serve as the gate dielectric.
- Spin coating or flexo / inkjet printing of the nitrate precursor.
- Annealing of the semiconductor at 300 °C for 30 min or at 200 °C for 15 min with FUV on a hotplate.
- Evaporation of the Al source and drain electrodes using a metal shadow mask for 50 μm channel length.
- Post annealing of the devices at 150 °C for 30 min on a hotplate.

- Star map shown at LOPE-C 2014
- on-off circuit and LED driver on glass
- 3 discrete LEDs
- Enfucell flexible battery
- See video

Flexography-printed In$_2$O$_3$ TFTs on PI plastic

- Electronic properties of In$_2$O$_3$ TFTs annealed at 300 °C:
  - Optimized process gives $\mu_{\text{sat}} = 8 \text{ cm}^2/(\text{Vs})$ on average and $V_{\text{on}} \sim 0 \text{ V}$

High-performance oxide devices with flexographic printing on plastic

- "Flexography-Printed In$_2$O$_3$ Semiconductor Layers for High-Mobility Thin-Film Transistors on Flexible Plastic Substrate", J. Leppäniemi et al, Advanced Materials, 2015, 27, 7168–7175 http://dx.doi.org/10.1002/adma.201502569

02/02/2017
Case ROPAS: Hybrid solution on paper

Henrik Sandberg, Liisa Hakola, Elina Jansson, Arttu Huttunen, Maria Smolander
## ROPAS demonstrators

### Target on logistics

<table>
<thead>
<tr>
<th>Security tag</th>
<th>Smart label</th>
<th>Smart Envelop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shipping of valuable goods</td>
<td>Shipping of precious goods</td>
<td>Registered post</td>
</tr>
<tr>
<td>Open/close detection</td>
<td>Humidity and temperature sensor</td>
<td>Track and trace Password control</td>
</tr>
</tbody>
</table>

- Shipping of valuable goods
- Shipping of precious goods
- Registered post
- Open/close detection
- Humidity and temperature sensor
- Track and trace Password control

![Security tag](image1.png)  
![Smart label](image2.png)  
![Smart Envelop](image3.png)
Demonstrators

- **Security Tag**
  - Conductive tracks
  - Components placing

- **Smart label**
  - Chip integration
  - NFC integration
  - Printed sensors

- **Smart envelope**
  - Smaller print features
  - Antenna integration
  - ICT (Security / password)
Process up-scaling

- Three main technologies
  - Conductive tracks and dielectrics
    - Printing
      - Screen, FLEXO, Inkjet
    - Hot foil transfer
  - Postprocessing
    - Thermal, UV, IR, Flash sintering
  - Integration
    - Heterogeneous & monolithic
  - Encapsulation / packaging
    - Lamination, overcoat, inlay
VTT: MAXI & ROKO PRINTING

Anilox Plate

Camera for registration

Paper

Circuit (MAXI)

Dielectric (MAXI)

Antenna & bridges (ROKO)
Integration of components

- Direct printing of resistors (~4 kΩ)
- Reel-to-reel pick'n'place process in “stop- and- go“ mode
Security Tag

Shipment OK:

Shipment opened:
Smart envelope – track and trace

Wireless communication

Electronic layout

Envelope Design

Antenna performance

Web access and security
MATERIALS & METHODS

- R2R printing of circuit, dielectric, and antenna layers
  - Registration to circuit layer
  - All the layer have different register marks
  - Visual marks and marks for automatic system
BRIDGE PRINTING

- Bridges were conductive
  - $0.26 \pm 0.01 \, \Omega$ (8 mm distance)

- No shorts (yield 100%) were detected
ANTENNA PRINTING

- Antenna structure was nicely reproduced
- Low square resistance value was obtained, < 9 Ohm
- Layer is rather rough and uneven

<table>
<thead>
<tr>
<th>Ink</th>
<th>Thickness (µm)</th>
<th>$R_a$ (nm)</th>
<th>$R_q$ (nm)</th>
<th>Spreading (µm)</th>
<th>Square resistance (mΩ/□)</th>
<th>Volume resistivity (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antenna</td>
<td>18.1 ± 2.8</td>
<td>3020 ± 520</td>
<td>3710 ± 660</td>
<td>50</td>
<td>14.8</td>
<td>2.7E-05</td>
</tr>
</tbody>
</table>
Component placing

• Pick’n’place process at VTT (Oulu site)
  – 23 basic two terminal packages
  – 1 oscillator
  – 1 chip
  – Flex integration:
    • Battery (enfucell)
    • Antenna (if separately printed)

• Main challenges
  – Number of components → e.g. ST adhesive is slow
  – Types of components → need for different types of adhesives
Smart Envelope

Patent application: EP 13176531.5
Printed paper based diagnostics

Maria Smolander, Liisa Hakola, Tuija Teerinen, Kaisa Kiri
Printed visual indicators and diagnostic tests

- **Sensors that give indication on the state of an item or analyte concentration by visual colour change or appearance**

- Printing methods for cost-efficiency, high throughout and integration into products

- VTT expertise in development of inks and materials (e.g. enzymes), optimisation of manufacturing process and up-scaling from laboratory to pilot scale

- Demonstration of food quality, health & well-being and environmental indicators
Paper-based diagnostics

- Simple design and low-cost
- Portable, flexible, disposable and bio-compatible
- High throughput in manufacturing can be achieved
- Reproducible with high sensitivity and accuracy
- No need for professional medical personnel or complicated instruments

- Potential for integration of high-density detection systems into a small device

Fluidic structures formed into chromatography paper (a) and clean room paper (c) by flexographic printing 5 w% polystyrene in xylene.

Flexographically printed fluidic structures in paper.
Olkkonen J, Lehtinen K, Erho T.
Printed and coated biomolecules on fibre based products

- **Bioactive functionalitites** (such as enzymes or antibodies) deposited into fiber based structures
- Cost effective manufacturing by printing and coating
  - incorporated in different paper coatings
  - microencapsulated and screen printed
  - flexo printed
  - ink jet printed as distinct pattern

Savolainen, Anne; Zhang, Yufen; Rochefort, Dominic; Holopainen, Ulla; Erho, Tomi; Virtanen, Jouko; Smolander, Maria; Biomacromolecules, 12 (2011) 2008-2015.
Glucose test demonstrator

- Tesorb paper substrate (80 g/m², Tervakoski)
- Four layers printed:
  1. Flexography printed polystyrene (5 wt-%) layer for liquid guiding, both sides of paper
  2. Flexography printed PEI (polyethylene imine, 5 wt-%) layer for pH modification
  3. Inkjet printed pH ink (2 wt-%) layer for visual colour change
  4. Inkjet printed enzyme ink (glucose oxidase 5 mg/ml) for reaction with glucose
- Four demonstrators: different combinations of lab and pilot scale inkjet and flexography
Principle of glucose test

1. Analyte (glucose) pipetted

2. Liquid flow in channels to reaction spots containing pH dye and enzyme

3. Colour change from red to yellow due to analyte triggered enzyme reaction causing pH change

Pink area = channel boundaries

White areas = liquid channels
Onsite Detection of Cyanobacteria Toxins

Value proposition:
- Inexpensive and simple-to-use test kit for detection of cyanobacterial toxins in water
- Based on mass-manufacturing methods for cost-effectiveness and disposability

Competitive edge: Paper or polymer based immunoassay test specific for toxin producing cyanobacteria (microcystin, nodularin)

Offering: Test kit for cyanobacteria toxins with market potential defined

Outcome: Accurate results in short time, onsite testing, user friendly, cost effective

R&D infrastructure: Printing technology, laboratory and pilot scale equipment, upscale manufacturing process

Process: Manufacturing process

Channel printing → Addition of cell lysis reagents → Inkjet printing/dosing of Au-conjugate & antibodies → Sealing=Test strip → Sealing=Test strip → Covering → Graphics printing → Sample treatment, including external cell lysis (if needed) → Instruction of use → Integration = test → Packaging = Test kit
Prototype for Cyanobacter test
https://www.youtube.com/watch?v=WhgwaOS_ek
Printed biofuel cell

Saara Tuurala & Maria Smolander
Operating Principle of Biofuel Cell

- Chemical energy of organic substrate (e.g. sugar or alcohol) is transformed into electricity via **biocatalysis** (by enzymes or living cells).
- The use of enzymes as catalysts for the power source enables:
  - operation in mild conditions
  - use of renewable chemicals as fuel
  - disposability
- VTT’s printed biofuel cell – biobattery – uses glucose and air as fuel
- The biobattery produces µ-power; typically 1 µA/cm² at 0.5 V
Development Path of biobattery / microcurrent patch

Half enzymatic, printed power source

Fully enzymatic, printed power source

Cosmetic patch in industrial sheet-to-sheet process


Characterization and Stability Study of Immobilized PQQ-Dependent Aldose Dehydrogenase Bioanodes, S. Tuurala et al., Electroanalysis 24(2) (2012) 229-238

A mediated glucose/oxygen enzymatic fuel cell based on printed carbon inks containing aldose dehydrogenase and laccase as anode and cathode, P. Jenkins et al., Enzyme and Microbial Technology 50(3) (2012) 181-187

A comparison of glucose oxidase and aldose dehydrogenase as mediated anodes in printed, glucose/oxygen enzymatic fuel cells using ABTS/laccase cathodes, P. Jenkins et al., Bioelectrochemistry 87 (2012) 172-177

Production of bioactive electrode layers in R2R pilot scale


Increasing the Operational Lifetime of a Printed Enzymatic Power Source using Superabsorbent Polymers as the Anode Support, S. Tuurala et al., Energy Technology, online on September 2015

IPR

- US2009280408A
- US2013017457A
- WO2011073519
- WO15092153A1
- FI20155619
Application of the biofuel cell in microcurrent skin patch

- Biofuel cell based microcurrent patch facilitates the delivery of cosmetic substances efficiently into the skin
- VTTs microcurrent patch has following features:
  - efficacy shown by *in vitro* skin microscopy - increases the metabolic activity and density of collagen fibers of the skin
  - stability - can be stored in dry state even for years and is activated by moisture activation
  - environmentally friendly - is based on renewable, enzymatic cathodic catalyst
  - disposable - not interpreted as a battery according to the definition
Roll-to-roll printed biocatalysts for electrochemical application

Scale-up of manufacturing of printed enzyme electrodes for enzymatic power source applications

Anodic & cathodic layers of printed, enzyme-based biobattery printed and dried in ROKO pilot scale printing line

Saara Tuurala, Otto-Ville Kaukonemi, Leo von Herten, Johanna Uotila, Anu Vaari, Mikael Bergelin, Pia Sjöberg, Jan-Erik Eriksson, Maria Smolander, accepted to J Appl Electrochem, DOI 10.1007/s10800-014-0702-2

*ROKO pilot scale printing line
- 4 replaceable printing units
- Direct and reverse gravure, rotary screen, and flexography units
- Corona and lamination units
- Drying units (air, UV, IR)
- Web width 300 mm
- Max. web velocity 10 m/min
Environmentally friendly chemistry

- Unique environmentally friendly chemistry
- Cathodic catalysts is laccase enzyme
- Renewable, produced in biotechnical process
- Enables operation in mild conditions
- Enables disposability
Overall conclusions

- Several printing and hybrid integration methods have been successfully used for embedding electronic, chemical and biological functionalities into R2R processed, flexible substrates including paper
- Value addition of R2R processes due to flexibility, possibility for large area, cost effective production enabling high volume and disposable products
- Main focus to be selected according to concept and application, materials and process need to meet the specs
- Pilot scale trials to demonstrate the proof-of-manufacturability
TECHNOLOGY FOR BUSINESS