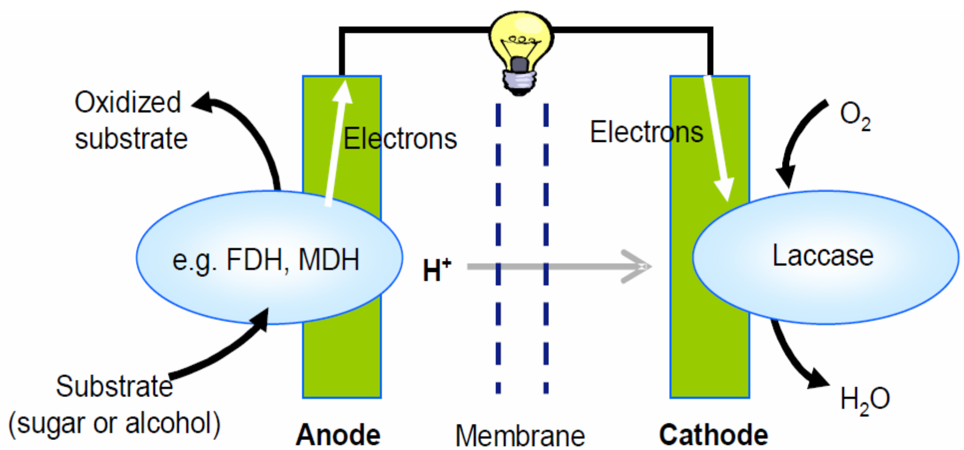
Printed biofuel cells



Presented by:

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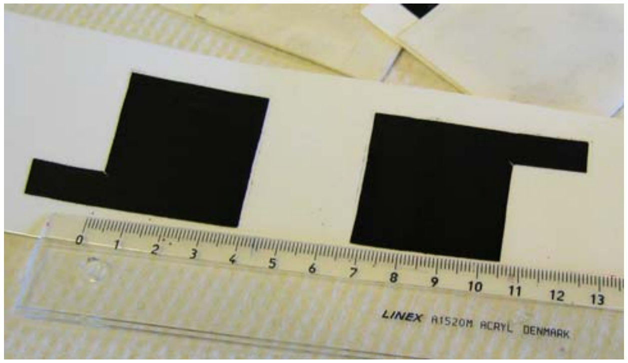
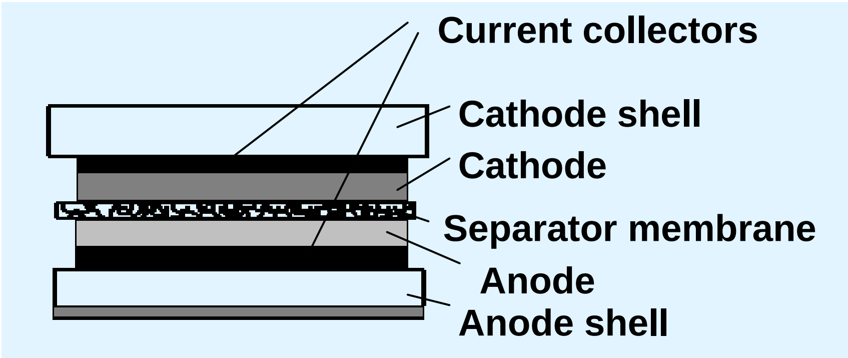
TAPPI people resources solutions

Printed biofuel cells
- Contents of the presentation

- Principle of the biofuel cell (BFC)
- Motivation
- Materials & testing methods
- Examples of BFC performance
- BFC with supercapacitor
- Manufacturing aspects

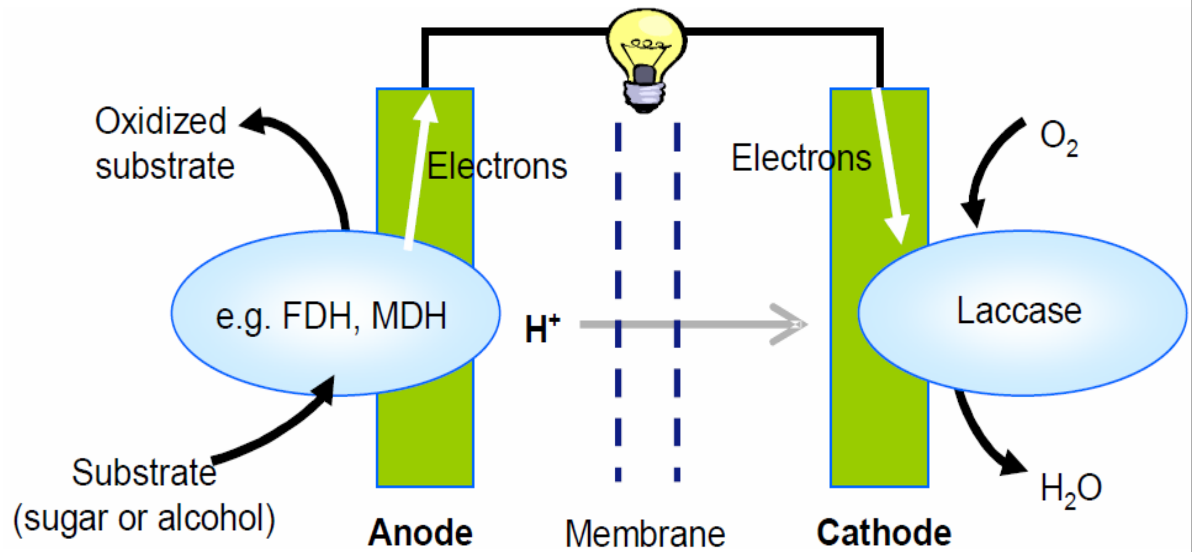




Printed BFC = layered structure (thickness 0.5 mm) composed of printed enzymatically active layers

Principle of Biofuel cells

- Chemical energy is transformed into electricity via **biocatalysis** (enzymes/living cells)
- Electron transfer takes place via direct (DET) or mediated (MET) electron transfer



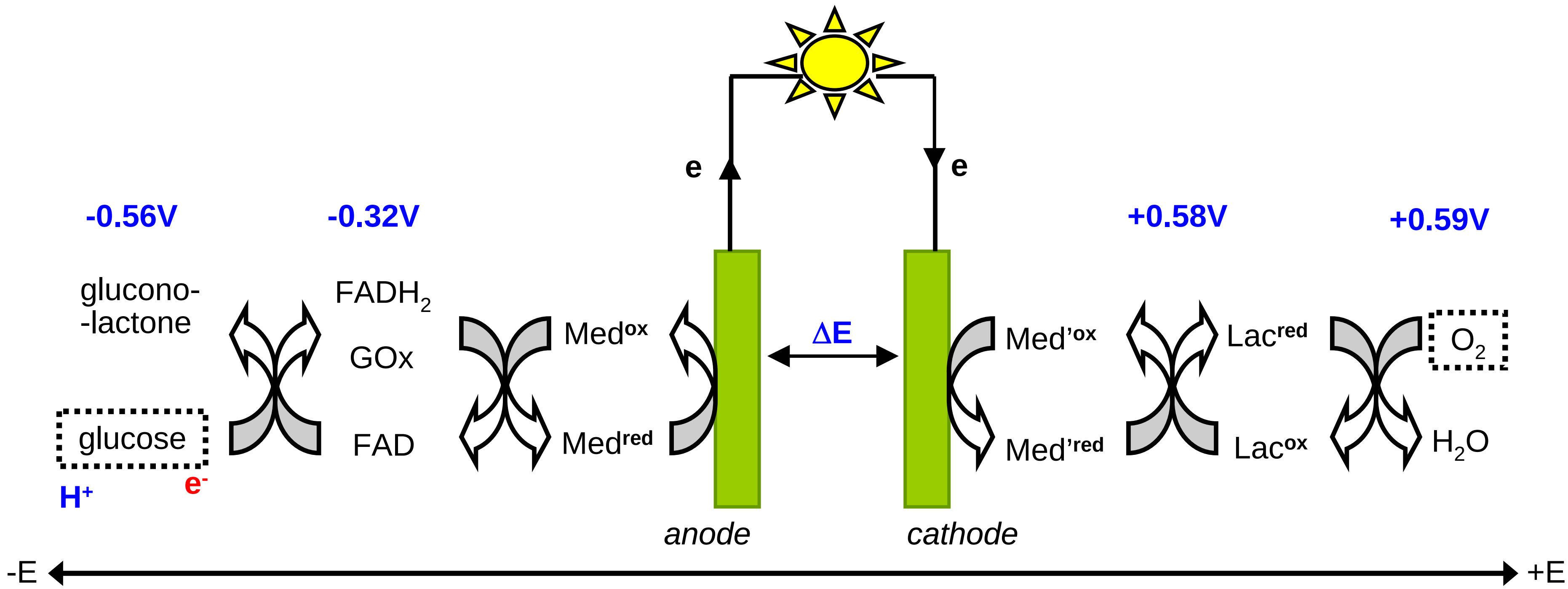
Anode compartment: Examples of oxidation

1. Methanol: $CH_3OH \rightarrow \rightarrow$ CHOOH + 4 H^+ + 4 e^-
2. Ethanol: $CH_3CH_2OH \rightarrow \rightarrow CH_3CHOOH$ + 4 H^+ + 4 e^-
3. Glucose: Glucose $\rightarrow$ Glucono lactone + 2 H^+ + 2 e^-

Cathode compartment: Examples of reduction

1. Oxygen: O_2 + 4 H^+ + 4 $e^- \rightarrow$ 2 H_2O
2. Hydrogen peroxide: H_2O_2 + 2 H^+ + 2 $e^- \rightarrow$ 2 H_2O

Example of biofuel cell based on glucose oxidase and laccase as anodic and cathodic catalytes



***GOx** : Glucose oxidase*
***Lac** : Laccase*
***Med** : Electron transfer mediator*

Individual fuel cells can be combined into a fuel cell "stack". The number of fuel cells in the stack determines the total voltage, and the surface area of each cell determines the total current.

Electron transfer in biofuel cells

Electron transfer (ET) between enzymes and electrodes plays the key role in performance of biofuel cells & biosensors
Possibilities:

(a) Direct ET at a bare or monolayer-modified electrode.

(b) Shuttle mechanism based on free-diffusing redox species.

(c) Electron hopping in a redox-relay modified polymeric hydrogel.

(d) ET via a conducting polymer chain.

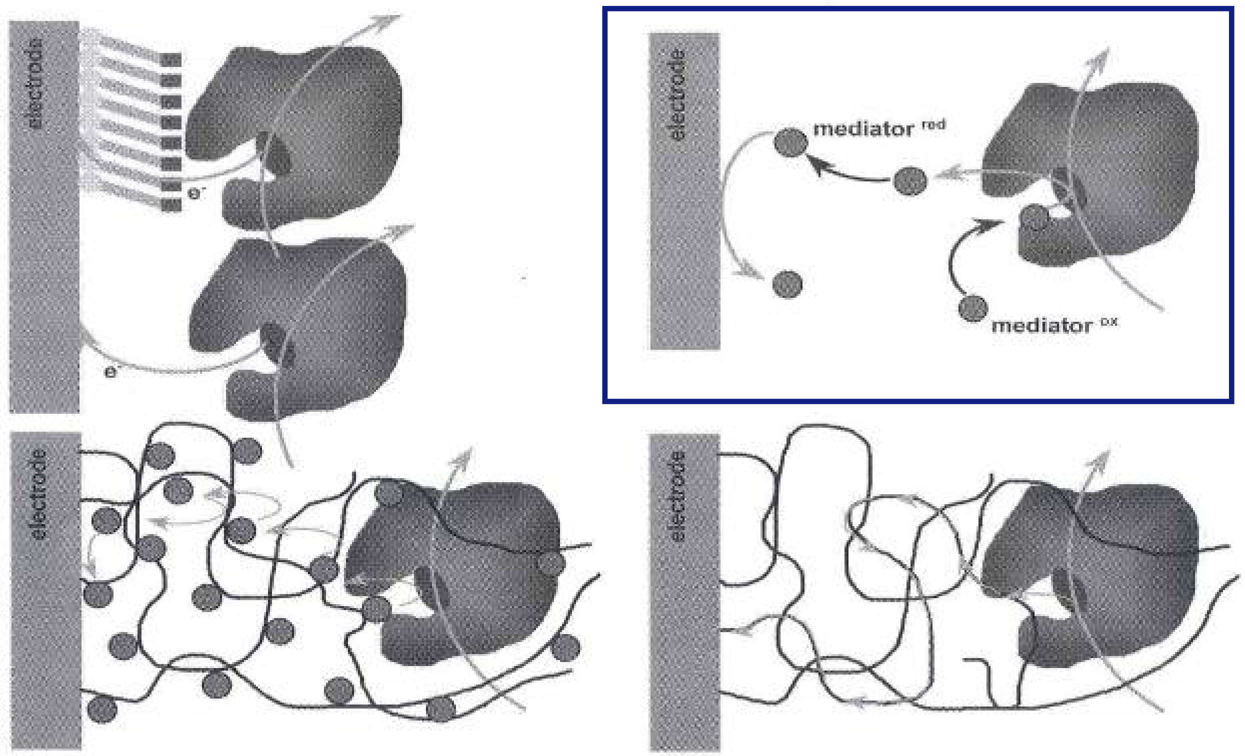
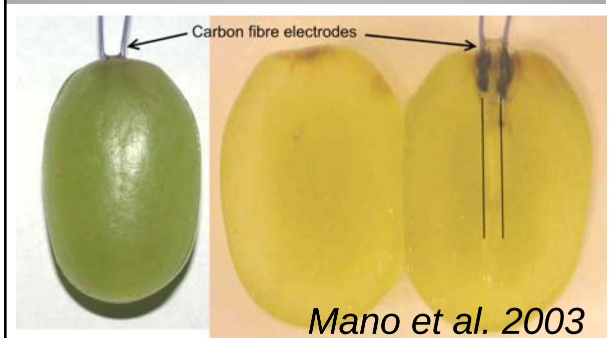


Figure by Schuhmann, 2002

Research on biofuel cells

Akermin

Sony



Mano et al. 2003

- Initiated in the 1960s, remarkable increase in the research activities since year 2000
- Cumulative number of publications till today is about 1800 (including appr. 1/6 patents)

- Remarkable actors in the field:
  - **Prof. Minteer et al.** (St. Louis University, Akermin)
    - enzyme stabilisation, power sources for portable applications
  - **Sony Corporation**
    - power sources for e.g. MP3 players and toys (highest reported biofuel cell power 50 mW)
  - **Prof. Heller et al**. (University of Texas)
    - miniaturised biofuel cells for diagnostic applications

Motivation for printed BFC

Predicted growth of disposable electronics market by 2015 *

- Inexpensive printed RFID tags e.g. for smart packaging **$12.4 billion**
- E-paper displays sold for point-of-purchase applications **$1.6 billion**
- New products “games, gadgets and gizmos” based on printed and/or organic electronics **$1.2 billion**.

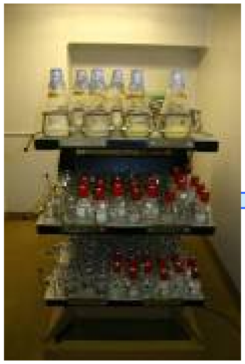
Photos: Hitachi, Fujitsu, Wikipedia

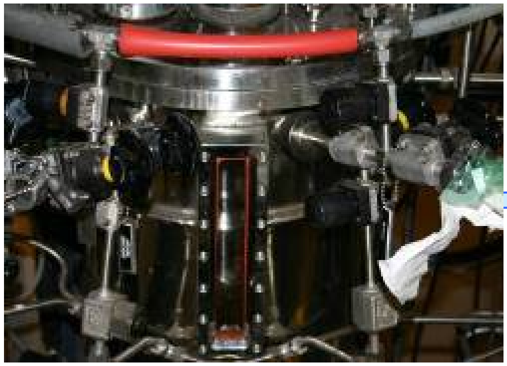
Prediction > 15 billion US$ business

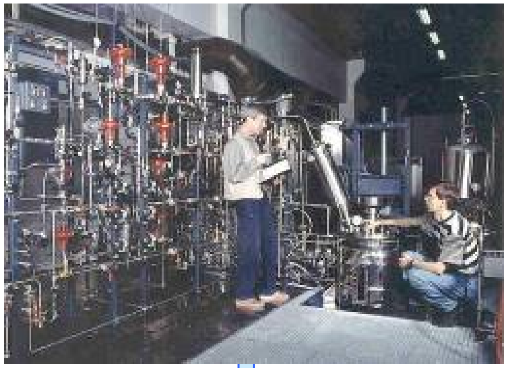
Disposable electronics forms a remarkable application area for printed, mass-manufactured power sources

**Nanomarkets, 2007*

Biocatalysts







Production in pilot scale facilities

300 L Fermenter

Down stream processing

CATHODE

- Laccase from *Trametes hirsuta (ThL) (high redox) & Melanocarpus albomyces (recombinant) (low redox)**

ANODE

- PQQ-dependent aldose dehydrogenase from *Gluconobacter oxydans (ALDH)*
- Glucose oxidase from *A. niger (commercial)*

Hakulinen et al. 2002. Nat. Struct. Biol. 9, 601-605

Printed biocatalytic layers

Biocatalytic conducting ink
- conducting carbon based matrix (commercial, experimental), biocatalysts & mediators*

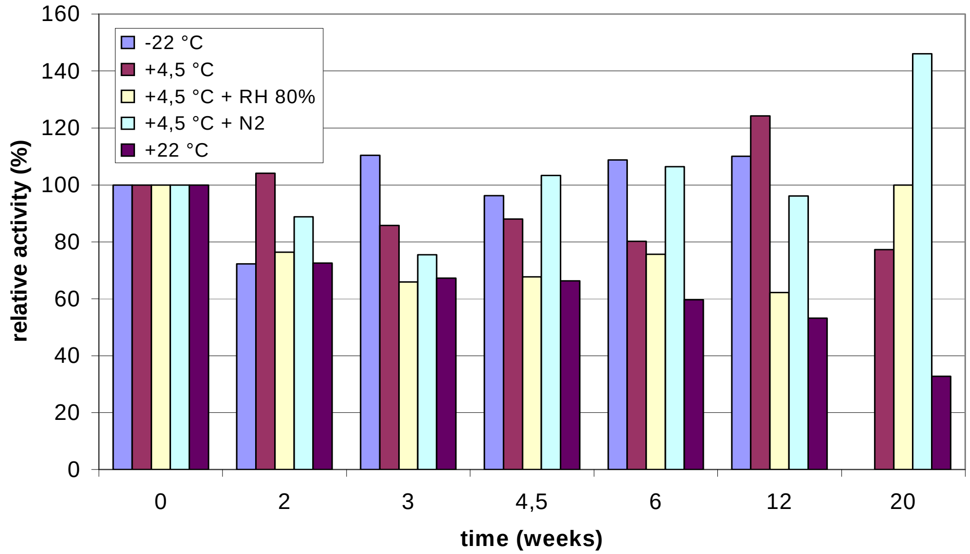
Printing or coating
- K Hand Coater, RK Print Coat Instruments LtD
- screen printing, batch (mesh 30 cm-1)

Functional layers
- Dry weight appr. ~ 0.002 g/cm^2
- Enzyme amount appr. **1 nkat / cm^2**

Fuels
- oxygen – diffusion through cell enclosure
- glucose – added to the cell on one go

Electrolyte
- Potassium phosphate pH 5

Separator
- cellophane, dialysis membrane, paper

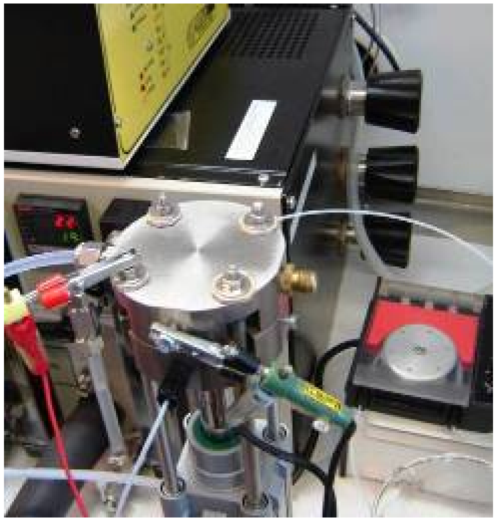


Printed catalysts stored at +4°C. Stability of prints during storage evaluated measuring enzyme activity by monitoring O_2 reduction by luminesence quenching (cathodic activity maintained for months, anodic activity for weeks)

**Ink compositions*

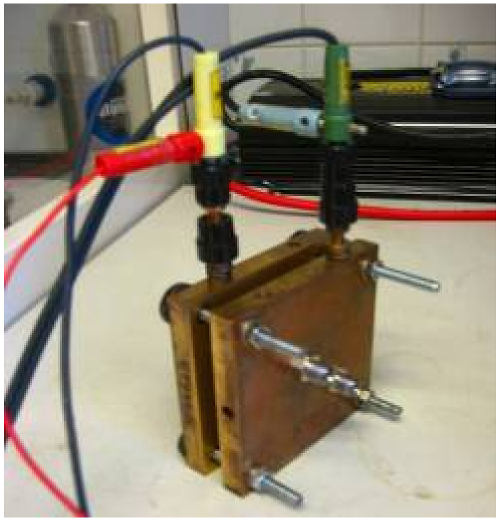
	Anode	Cathode
Enzymes	▪ Glucose oxidase **GOx (Sigma)** ▪ Aldose dehydrogenase **ALDH** (VTT)	▪ *Trametes hirsuta* laccase ***ThL* (VTT)** ▪ *Melanocarpus albomyces* laccase ***rMaL* (VTT)**
Mediators	▪ Tetra methyl-p-phenylenediamine **TMPD** ▪ Ferrocenemethanol **FeMeOH** ▪ Hexacyanoferrate(II) **$K_4Fe(CN)_6$**	▪ 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) **ABTS**

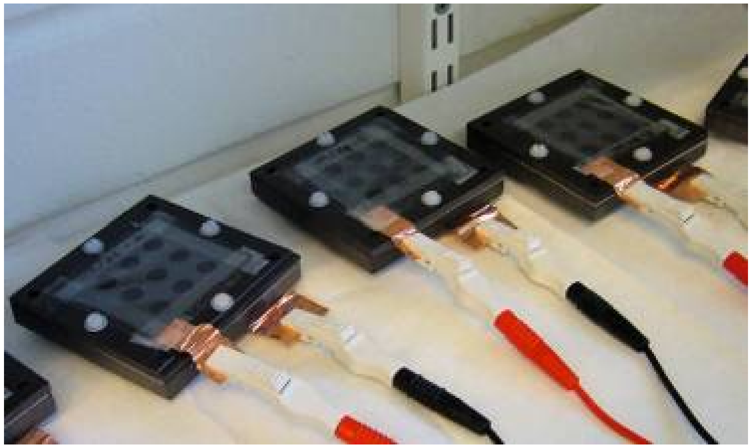
Performance testing hardware of printed power sources



Cell with Fuel and Air feed

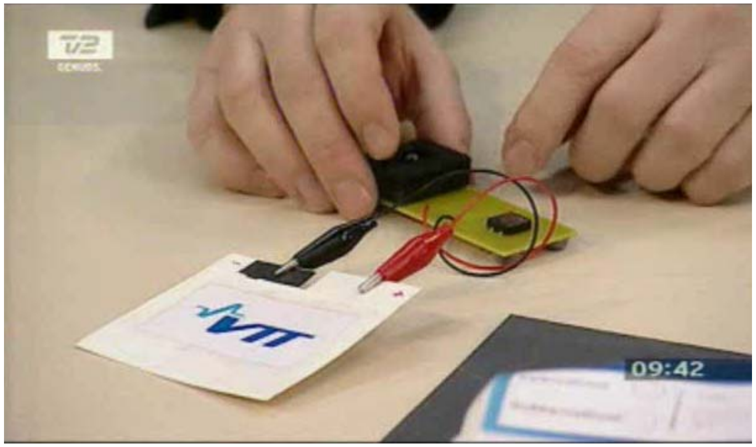
Cell with Closed Anode





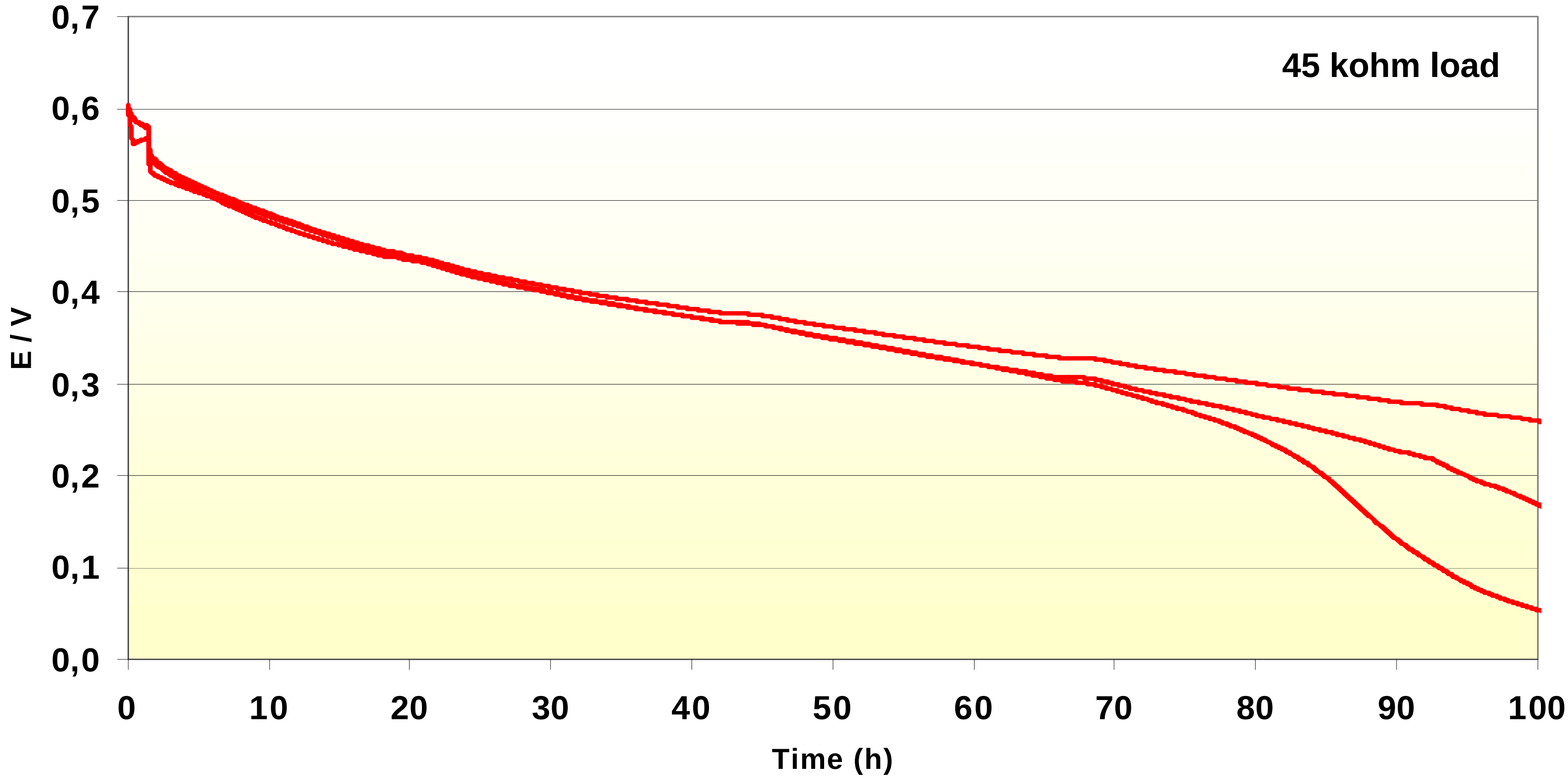
- $12\ cm^2$
- Solid anode
- Free breathing cathode
- 20 parallel measurements

Graphite plate stand alone



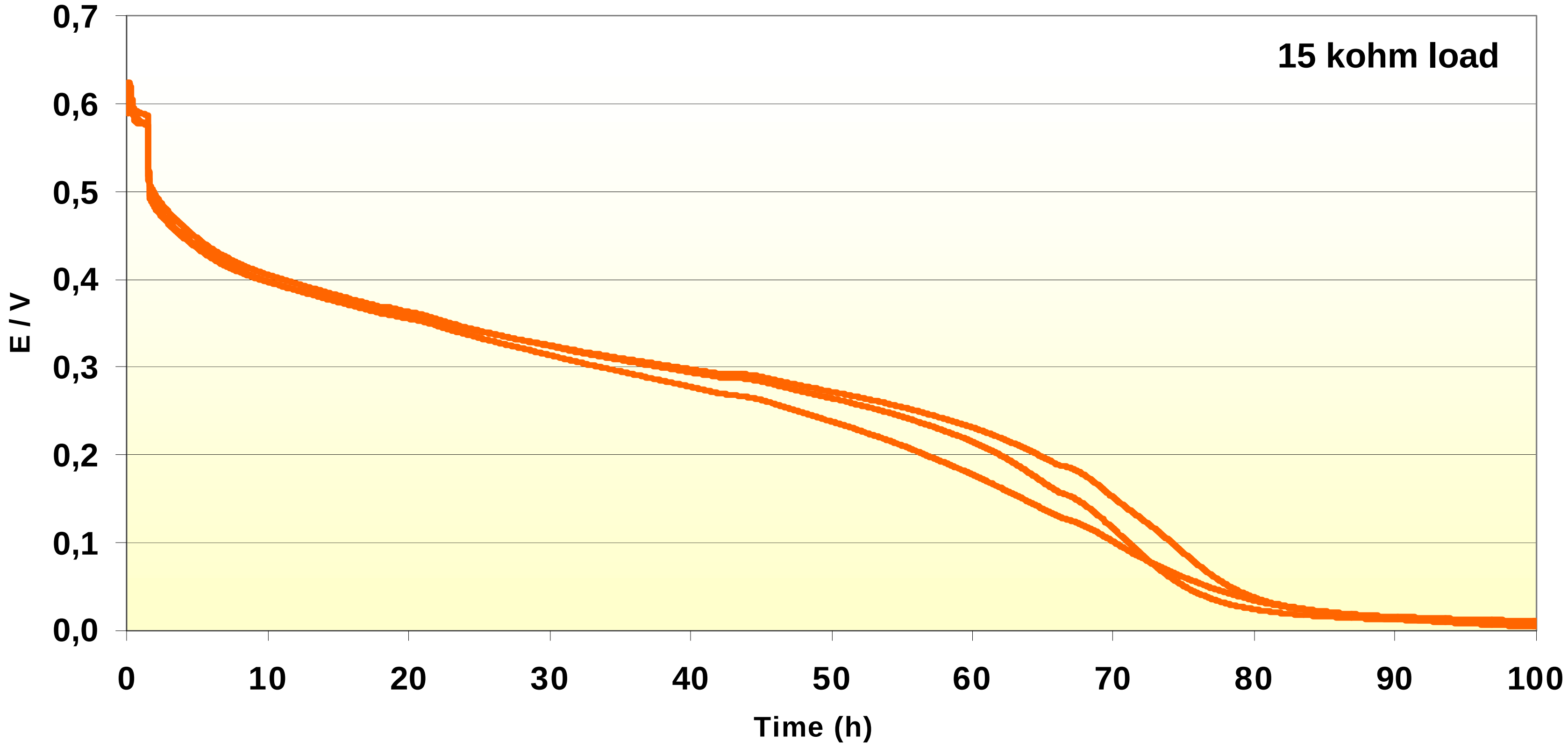
Paper board stand alone

Typical performance of the printed biofuel cell



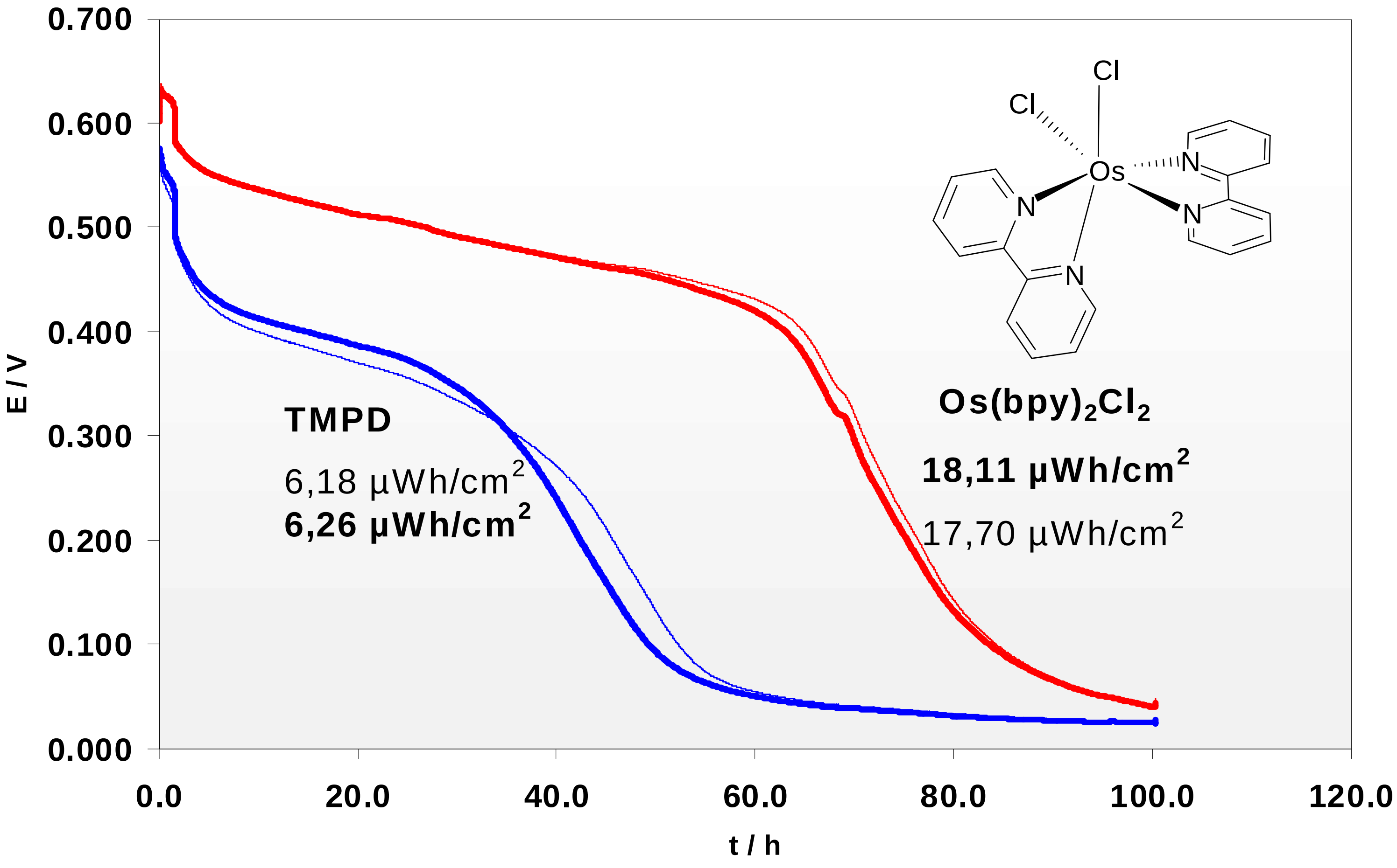
Cathode: *Laccase from Trametes hirsuta (ThL) (mediator ABTS)*
Anode: *Aldose dehydrogenase (ALDH) from Gluconobacter oxydans (mediator TMPD)*

Typical performance of the printed biofuel cell



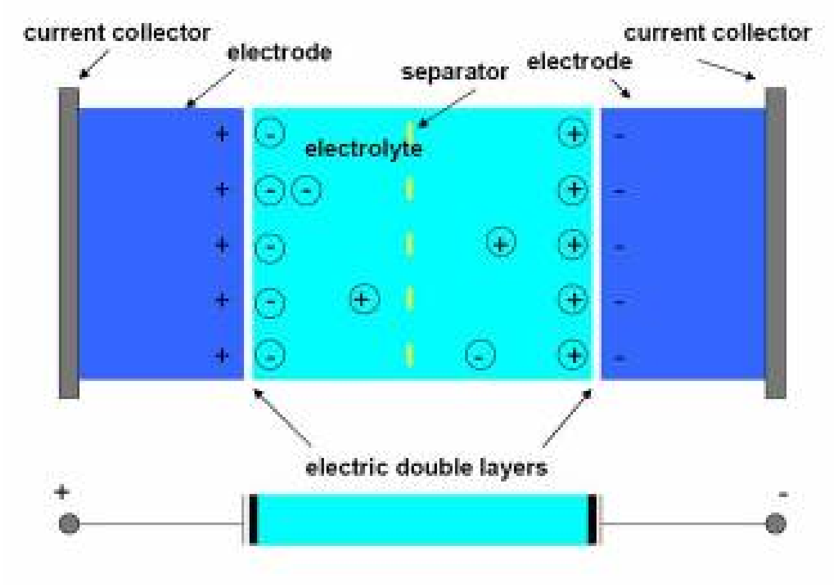
Cathode*: Laccase from Trametes hirsuta (ThL) (mediator ABTS)*
Anode*: Aldose dehydrogenase (ALDH) from Gluconobacter oxydans (mediator TMPD)*

Improvement of cell performance with novel anodic mediators



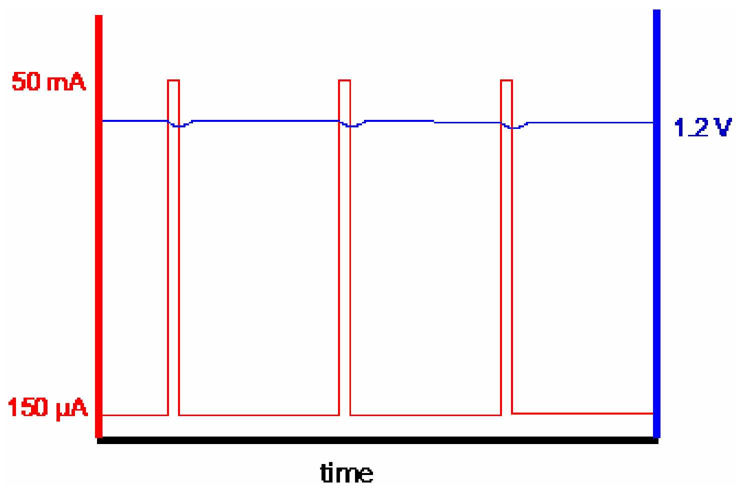
- Considerable increase in the cell performance could be obtained by using $Os(bpy)_2Cl_2$ instead of TMPD as the anodic mediator (ABTS used as the cathodic mediator)

Printed Supercapacitors to increase the momentarily power output of the BFCs



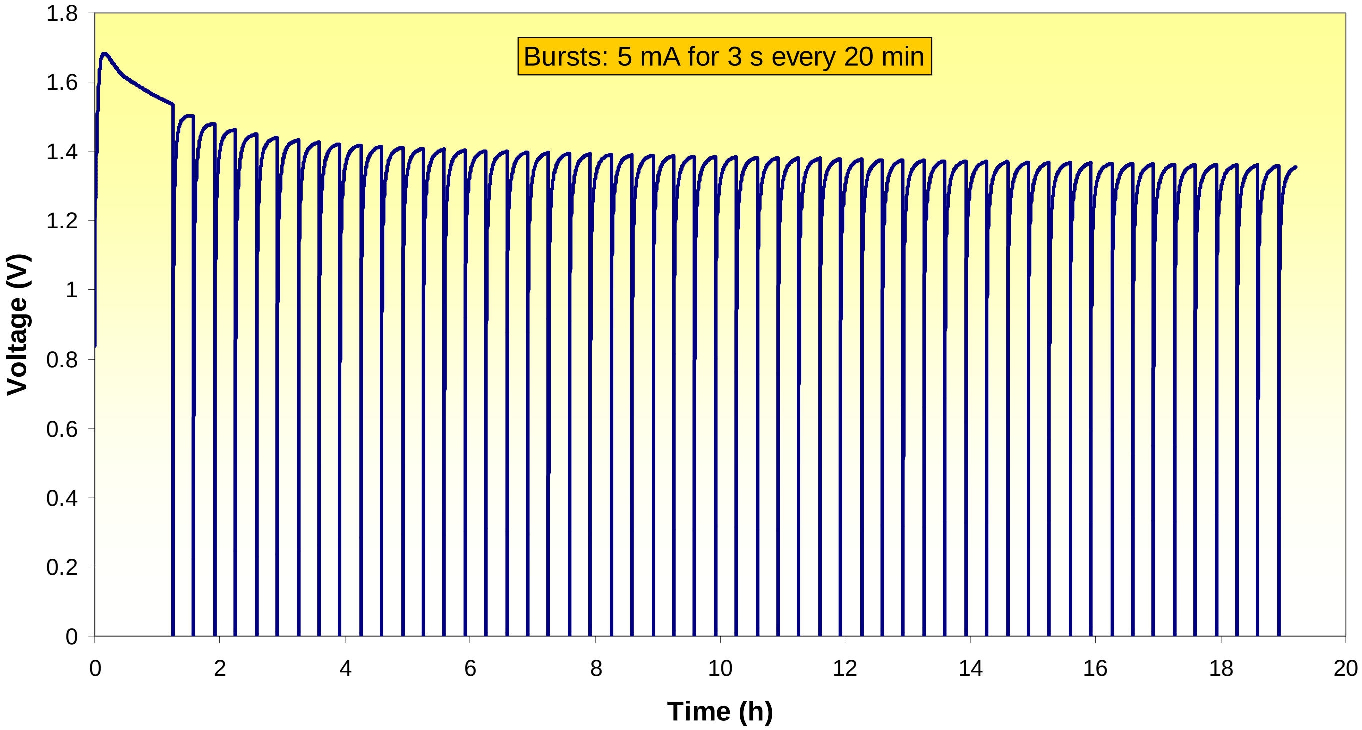
Supercapacitors with biofuel cell
- Increase the power level
- Can be printed simultaneously with biofuel cell
- Applicable also with other principal power sources

Structure
- Current collectors made from conductive ink
- Separator and electrolyte quite similar to those used in biofuel cell
- Porous electrodes are obtained from activated carbon ink



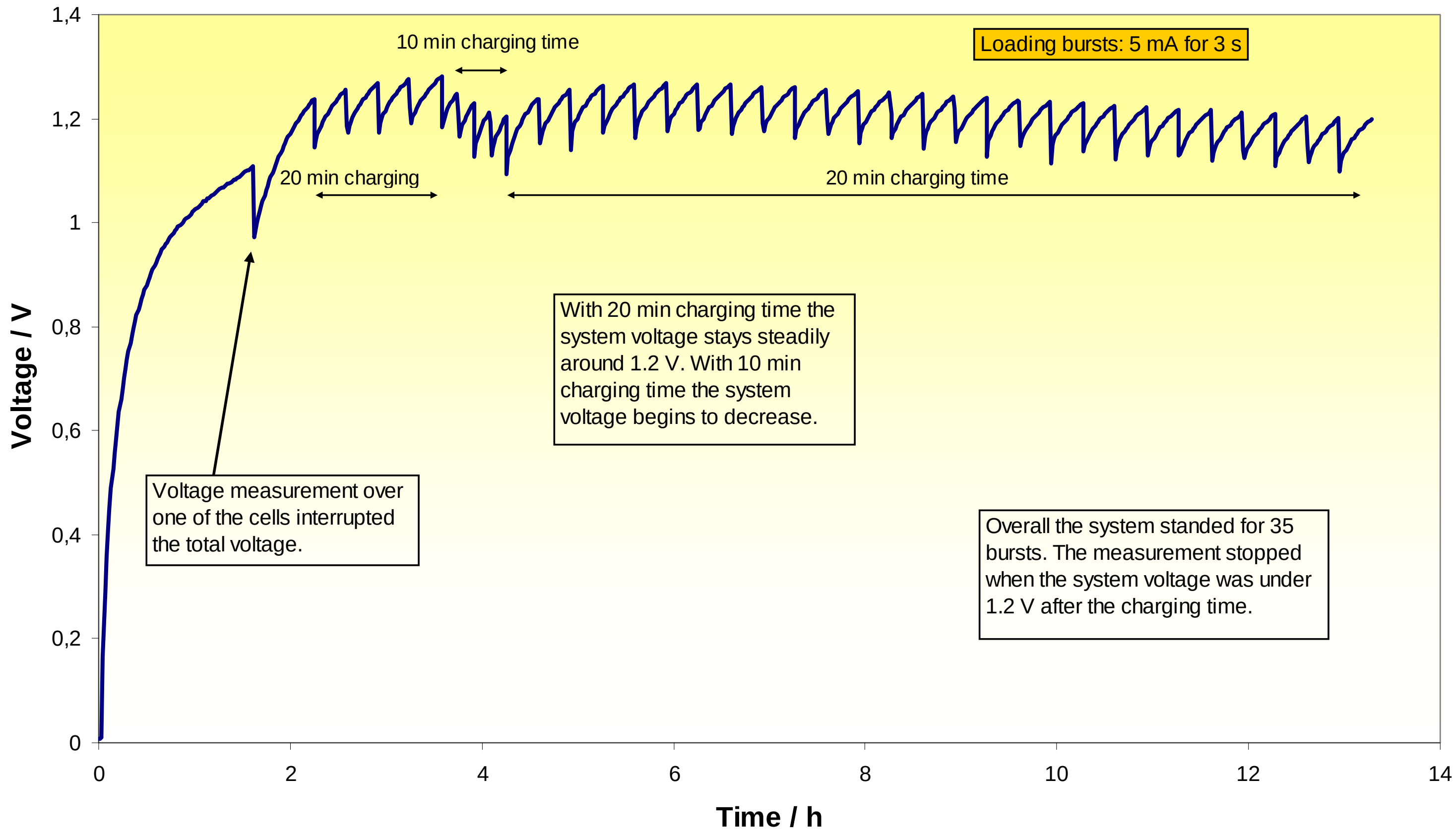
Integration of BFCs and supercapacitors

- 3 ALDH based printed BFCs connected in series
- Current burst of 5 mA for 3 s was withdrawn every 20 minutes
- Without supercapacitor
  - cell voltage down to 0V during every burst
  - open circuit could be maintained for several hours

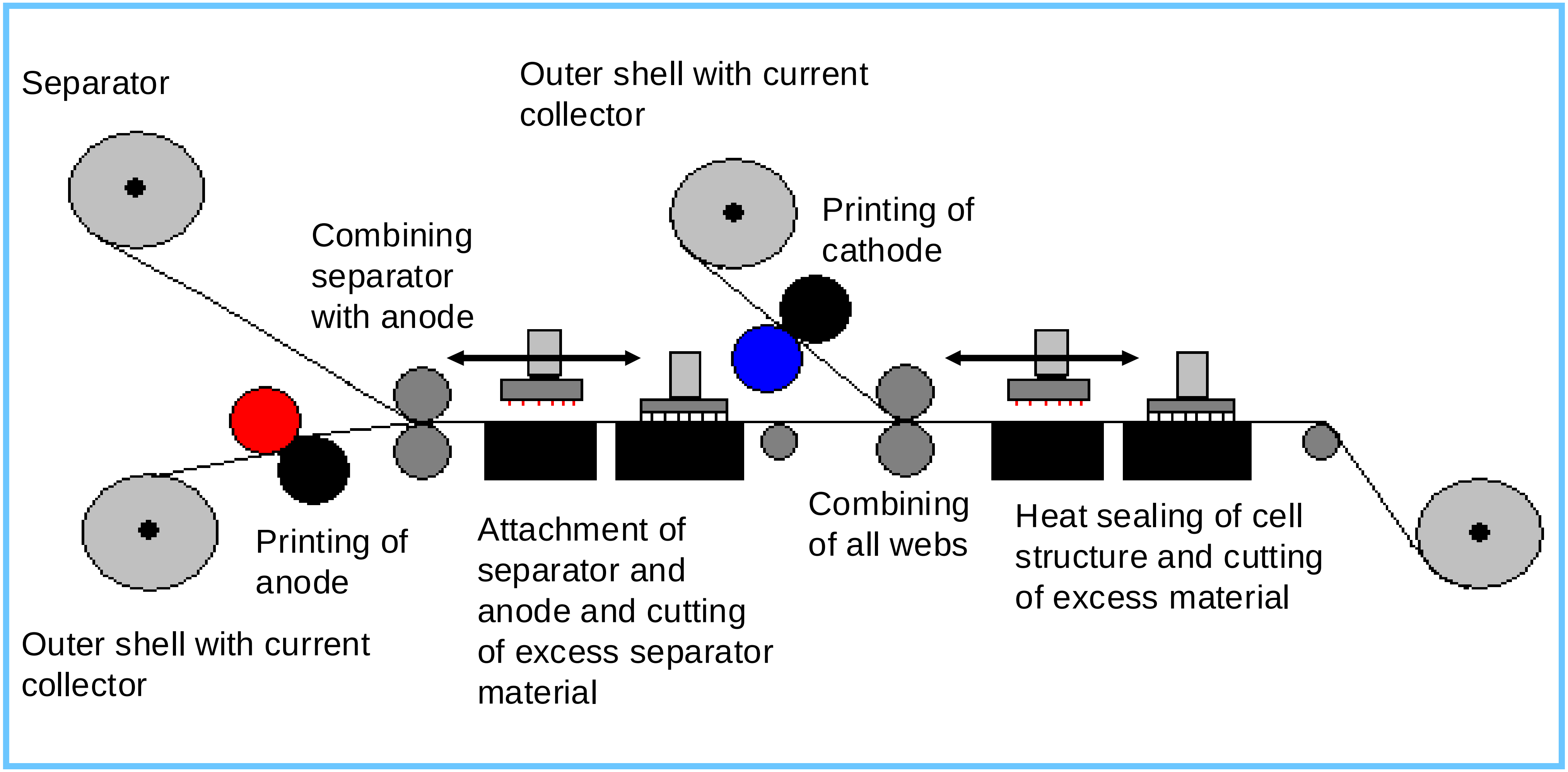


Integration of BFC with commercial supercapacitor

- With commercial capacitor (0.16 F) connected in parallel with the BFC array the cell voltage could be maintained above 1.2 V for 35 bursts



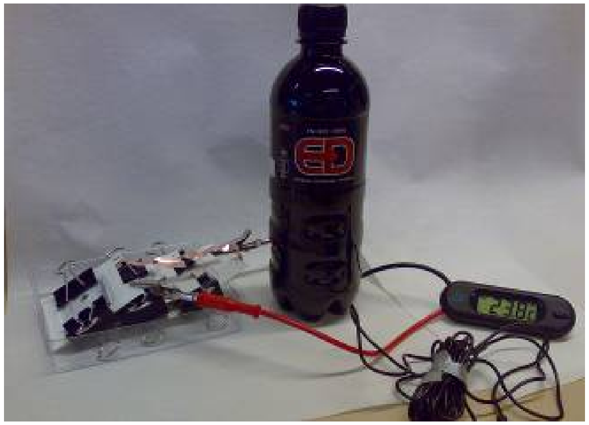
Schematic presentation of R2R manufacturing of a printed fuel cell



Material costs for printed power source

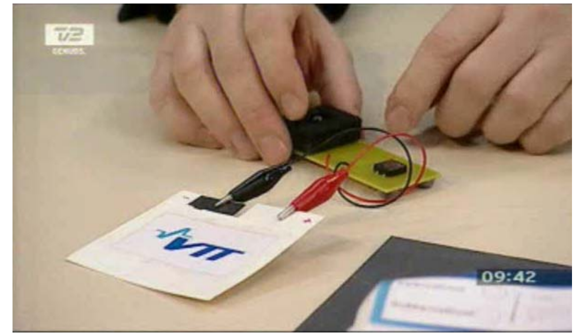
Material costs for 4 cells in series (8 cm^2 each)	price (€ cnt)	% of total
Current coll (anode), (5 mg/cm^2)	0.28	6.25
Carbon ink (anode), (4 mg/cm^2)	1.6	37.5
PE –coated cardboard	0.024	0.6
Dehydrogenase (1 $nkat/cm^2$)	0.24	5.6
Anodic mediator (TMPD), (0.02 mg/cm^2)	0.064	1.6
Separator	0.01	0.3
Electrolyte	negligible	0
Laccase (1 $nkat/cm^2$)	0.016	0.3
Cathodic mediator (ABTS), (0.08 mg/cm^2)	0.16	3.1
Carbon ink (cathode), (4 mg/cm^2)	1.6	37.5
Current collector (cathode), (5 mg/cm^2)	0.28	6.25
PE –coated cardboard	0.024	0.6
TOTAL COST:	**4.3 cnts**	99.6 %

Application of the Printed Biofuel Cell technology



Power source activation by the addition of fuel and/or moisture

Power source for digital thermometer and Light-Emitting Diode (LED) demonstrated

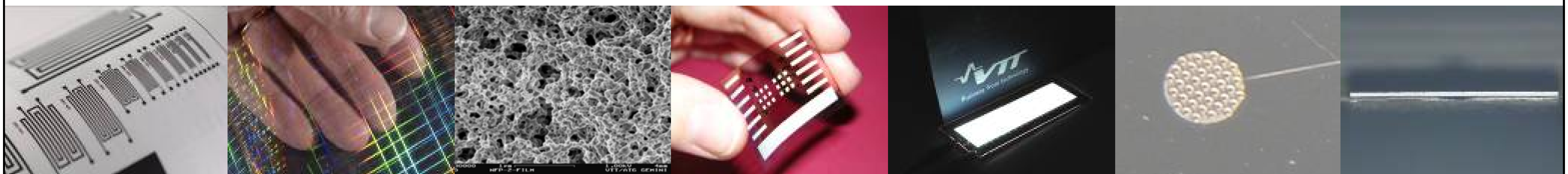


Potential application areas:

- active RFID tags (reading distance, memory, measurement)
- printed displays
- entertaining features in printed products (e.g. greeting cards)
- implantable sensors & diagnostic tests
- application of cosmetic products
- etc etc

Printed biofuel cells are enabling technology for many PE concepts promoting their disposability and sustainability.

Acknowledgements



- TEKES and EU FP6 for financial support
- Research partners & Industrial collaborators
- Co-workers throughout VTT

Thank you

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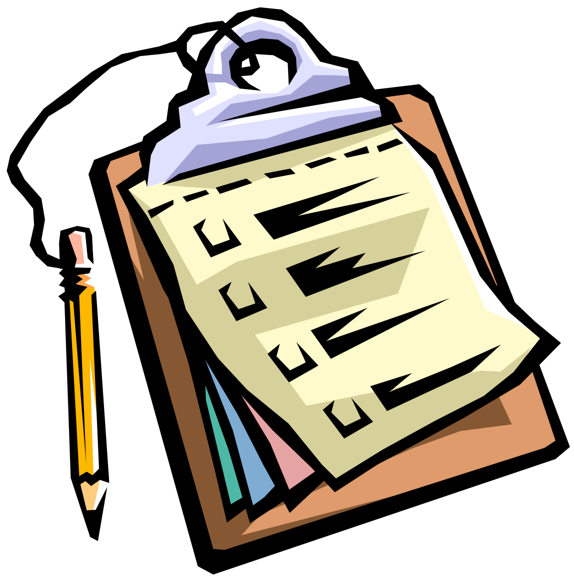

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