D1.7 – Patterning and printing performance assessment

Project acronym: **GREENBAT**

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1. Introduction

One of the main objectives of the GreenBAT project was to transfer the traditional lithium battery manufacturing process to printing line. Feasibility of this approach was studied both in laboratory and pilot scale.

Hereinafter, printed anodes and cathodes (CEA inks) are discussed, using VTT´s modular R2R ROKO machine. Next, NSMZ´s test printing prototype, based on standard R2R units, and adapted to single-sheet (possibly repetitive) printing, is presented. Finally, Imperial´s work on printable battery separators is introduced.

VTT´s ROKO printer is shown in Fig. 1 below. This roll-to-roll (R2R) printing machine can be equipped with different print units, including screen printing units, and it served for printing experiments in GREENBAT.

Figure 1. ROKO printing line

2. R2R screen printing of the anode and cathode

2.1 R2R screen printing of the anode

The main focus of pilot scale printing trials was to increase the thickness of the printed layers and study the ink behavior in continuous R2R printing process. This was achieved by printing several layers of aqueous anode ink on top of each other. Anode ink was printed on copper coated plastic substrate and calandered. Anode layer thickness greater than 110µ was achieved in 4printing passes.

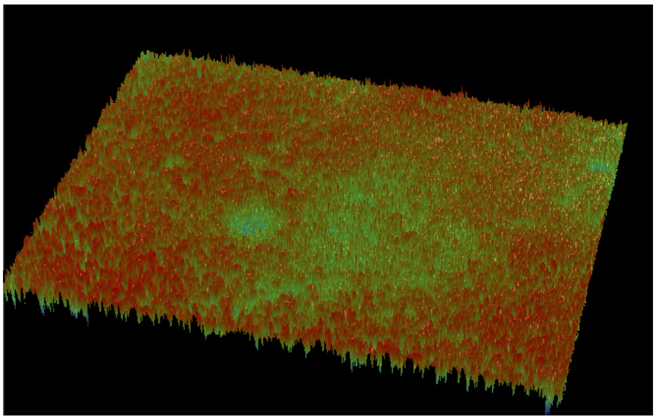

Figure 2. Surface of printed negative ink (4 layers) after calandering Mag: 5.2X (0.91 x 1.2 mm)

Printing of four consecutive layers results in relatively rough surface. However, the surface can be smoothened by separate calendaring step. Figure 3 represents a roll with printed anodes.

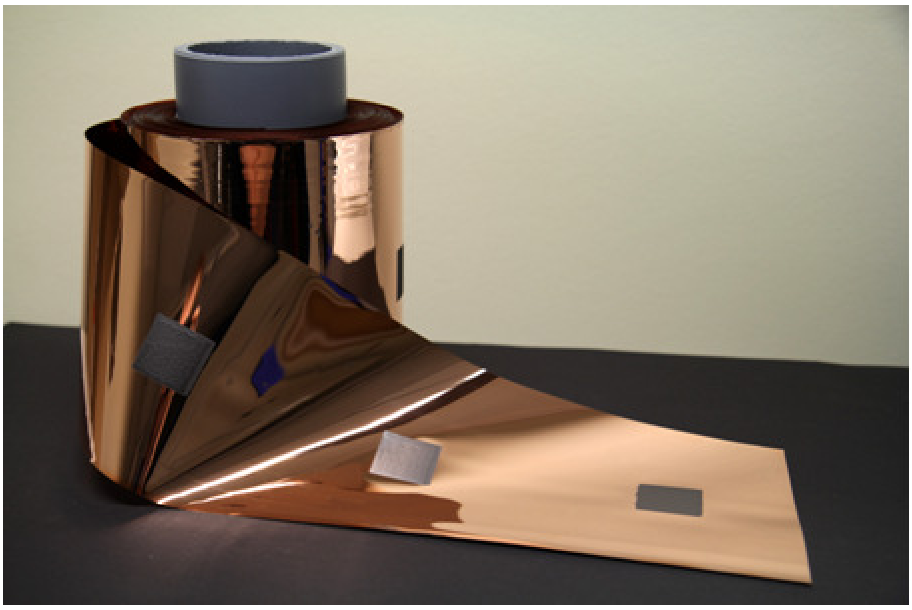

Figure 3. Roll of printed anodes.

2.2 R2R screen printing of the cathode

CEA Cathode ink was printed on evaporated Al substrate and further calandered. ROKO pilot printing machine equipped with two rotary screen printing units was used to print two layers of positive ink. Drying after each layer was done using at 120 ºC. Same print layouts were used as when printing the anodes.

Printability of ink was good. Printing of positive ink yielded thick and rough layer. Printing of two layers in one run succeeded, ink was drying well and registration was ok.

Adhesion of printed electrode layer improved after calandering. Print thickness after two passes + calandering was over 50 µm.

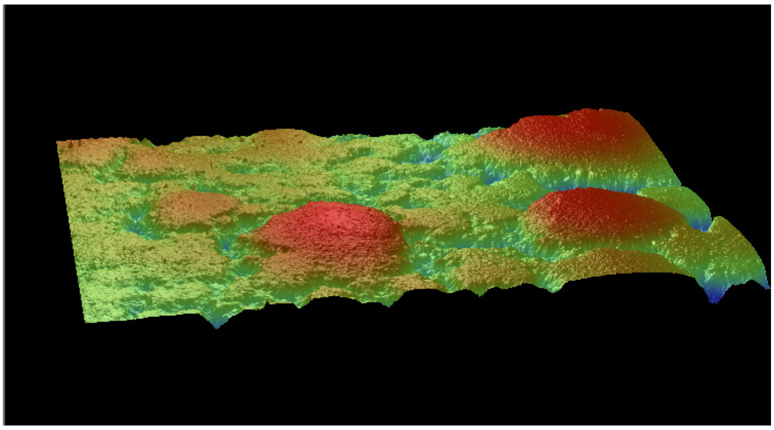

Figure 4. Surface of printed positive ink (two layers) after calandering Mag: 5.2X (0.91 x 1.2 mm)

As can be seen in the sample image the calandering process smoothens the printed surface considerably. Figure 5 represents a roll with printed cathodes.

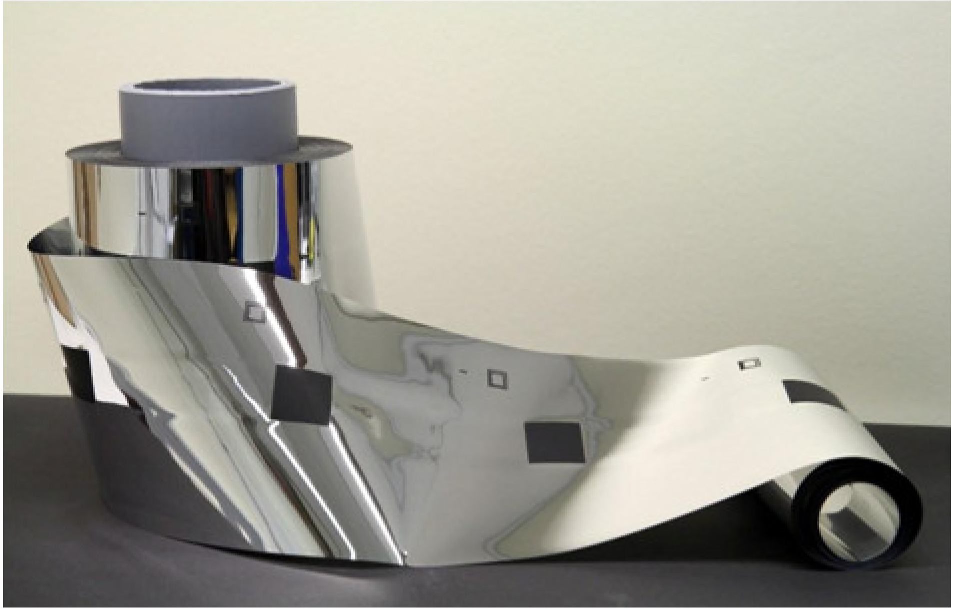

Figure 5. Roll of printed cathodes.

3. Experiments in repetitive printing on single sheets

To achieve thickness in a printing pattern, CEA had experimented before GREENBAT, e.g. printing 50 μ in 50 flexo-printing passes. Similarly, in experimental printing of battery electrode using the screen process, at least two printing passes would be used.

NSMZ set out to to design and build a flexo+ screen printing system that could support such registered multipass printing.

3.1 Achieving high flexo film thicknesses without patterning

Figs. 6 and 7 illustrates conventional-ink experiments at NSMZ, using a flexo process to deposit very smooth layers of 2μ thickness five times, for a 10μ final thickness.

Fig. 6 Flexo thick-film trial

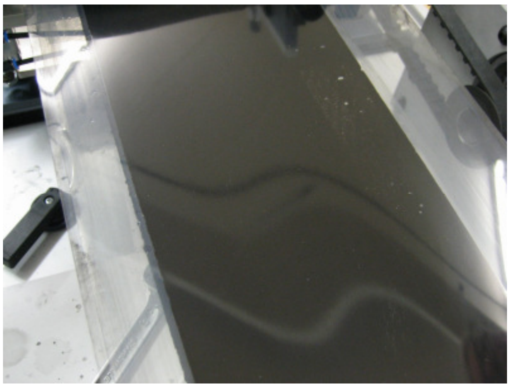

Fig. 7 Flexo thick film (unpatterned) ~ 2μ per pass

These experiments give an indication of the number of passes (i.e. of flexo print units) that would be needed in a production R2R machine. However, for GREENBAT or other electrode-printing applications, a pattern had to be printed. In the known art, with **n** printing passes and in an industrial roll-to-roll printer, **n** printing units would be needed, each with its own cliché, for such laboratory tests, which is totally impractical for (say) **n** > 5.

3.2 High thickness flexo printing under production conditions

In GREENBAT, NSMZ designed, built and tested a machine that would drive a production print unit, and a cylindrical substrate-holder in sync, so that single sheets could be printed in absolute production conditions.

Fig. 8 Overall machine + support.

Fig. 9 Control panel detail.

Figs. 8 + 9 show the design that was arrived at after several iterations. A standard NSMZ flexo unit is shown in the middle of the supporting table, and a cylindrical substrate support on the right. In-house analysis shows that this setup is capable of registering an ideal print cylinder and the substrate holding cylinder to **a few microns** precision, in its start-stop, single-sheet mode.

Results from actual wet-in-wet flexo tests are shown in Figs. 10 and 11 below, using conventional inks. On the left-hand side a single printing pass, on the right-hand side, a 20-fold over-print, in wet-in-wet mode. Fig. 10 featues a “large” flexo pattern, Fig. 11 a “small” one.

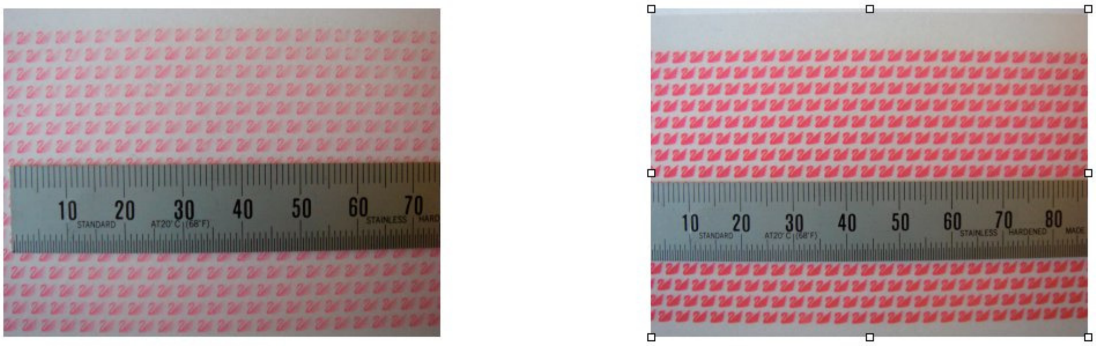

Fig. 10: Over-printing, wet-in-wet, large (about 2 x 3 mm) flexo patterns. Left, first printing pass. Right, 20th printing pass.

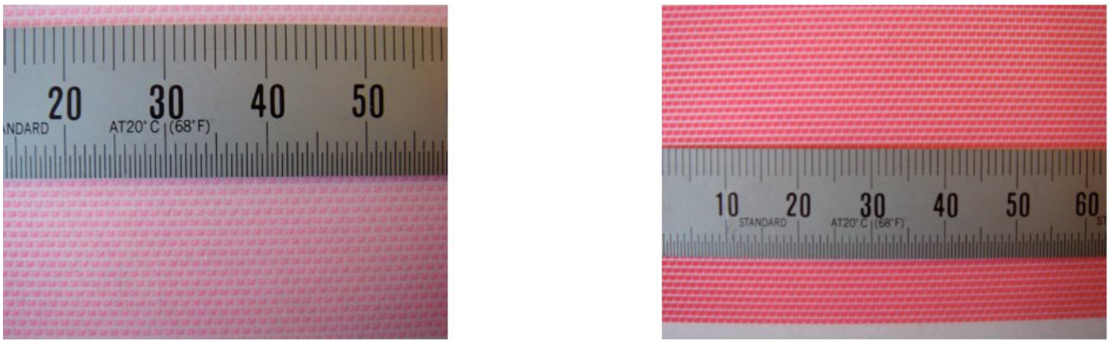

Fig. 11: Over-printing, wet-in-wet, smaller flexo patterns (~0,4 x 0,7 mm). Left, first printing pass. Right, 20th printing pass.

Fig. 11 shows that, even at the present stage, multiple-layer flexo printing of GREENBAT electrodes will be achievable. Improvements e.g. in substrate attachment are a next step.

Such technology is broadly applicable, and the NSMZ prototype is extensible in a variety of ways, e.g the substrate-holding cylinder could be coolable, or heatable, and due to its fully digital drive, it could feature an UV light source, and cure printed films between printing passes, in situ (i.e. without removing the substrate from the cylinder).

3.3 High thickness screen printing under production conditions

In the system shown in Figs. 8+9 above, the flexo unit may be substituted with a screen unit. This was trialed successfully using an NSMZ-built R2R screen printing unit. Fig. 12 below features a screenshot of a movie that shows repeated start-stop printing action with this machine, using a screen printing unit.

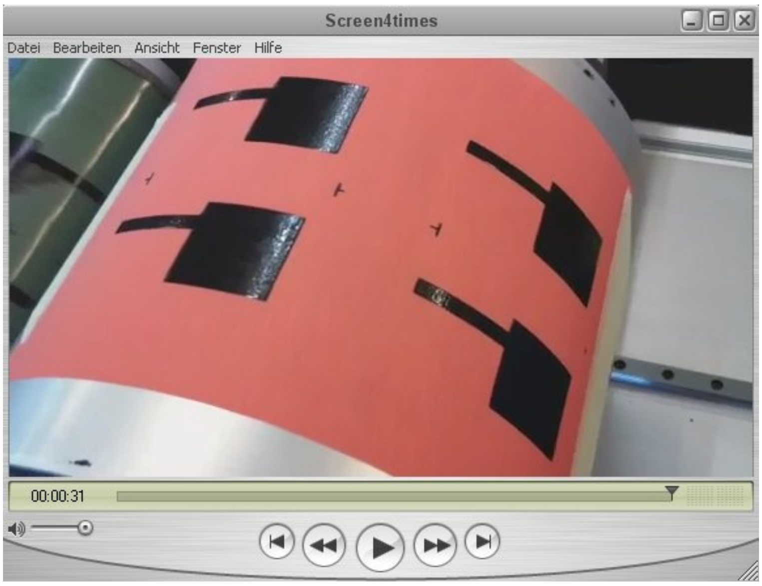

Fig. 12 Screenshot showing multiple screen printing using CEA ink and copper foil, four fold overprinting

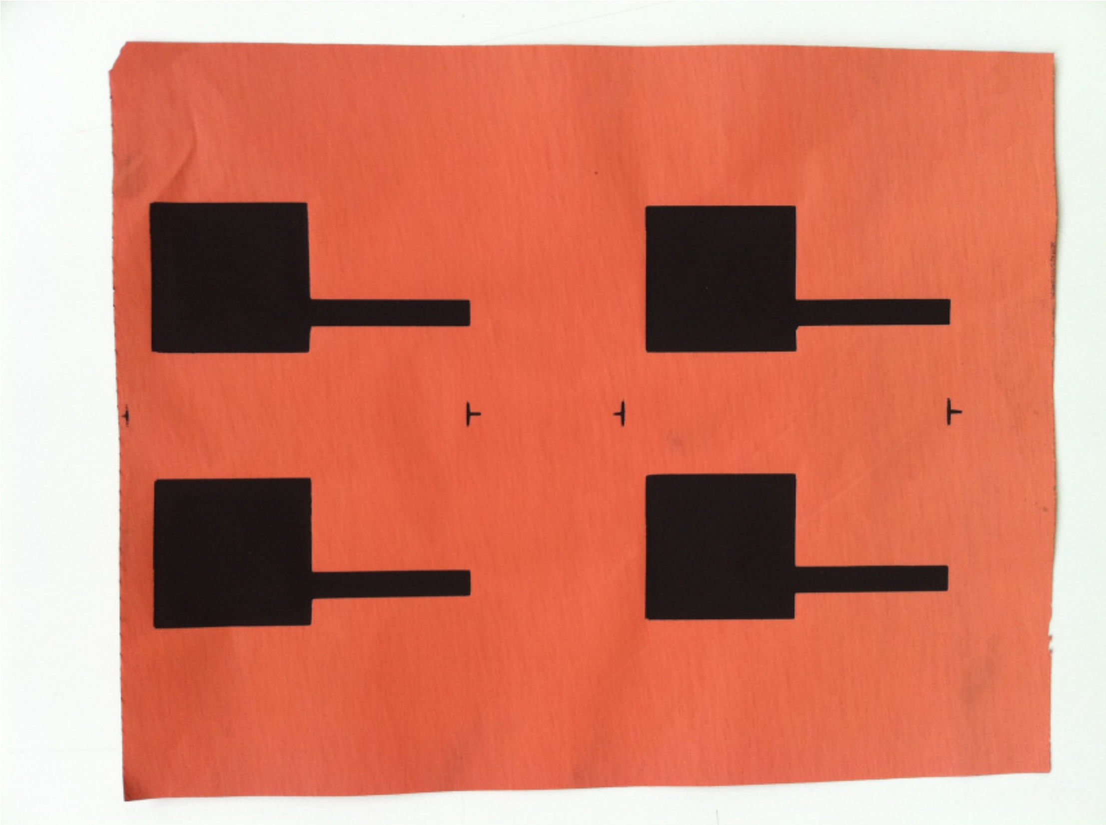

Fig. 13: Copper foil l after 5 printing passes and blow-drying.

However, all these experiments at NSMZ so far have the printing substrate sitting on a solid cylinder, as opposed to a R2R production situation, where said substrate would be stressed by the Web drive. This state of affairs was investigated by VTT.

4. Register accuracy and web dimension changes in roll to roll printing and laminating

In **traditional printing processes** sufficient colour register accuracy between different colours is typically between 50 – 100 microns, because human sight cannot observe smaller register errors. This means that printing presses are designed so, that this demand is met. However printed substrate undergoes dimension changes both in longitudinal direction (machine direction, MD) and in cross direction. MD expansion can be largely controlled by varying the image size for each printing unit, when material behaviour is known. Cross direction expansion is called fan-out and this can also be controlled by image size (only partly) and with special devices, which typically push the web in very narrow areas in several points across the web.

Considerable attention was given to registration, with very detailed basic studies and simulations conducted at VTT. NSMZ designed, built and tested a setup which basically adapted a R2R printer for registrated single-sheet printing, and in particular, for repetitive over-printing of the same pattern in up to 20 passes.

4.1 Substrate strain test method

Used PET foils in GreenBat project (thickness 76 µm) were coated with aluminium or copper (thickness 60 nm).

These plastics were tested with C-Impact device which has been designed and built in VTT, Figure 10.

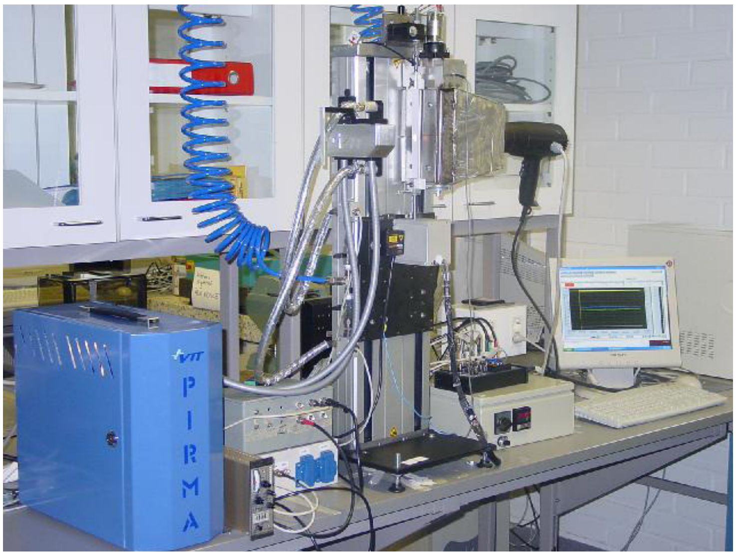

Figure 10. C-Impact apparatus

C-impact is specially made high speed stress strain testing apparatus. The maximum straining speed is about 1 m/s. Straining of samples can be programmed which enables cyclic testings.

Also creep (strain increase in constant tension) and relaxation (tension loss in constant strain) tests can be carried out with device. The test samples can be moistened and/or heated.

4.2 Results of laboratory scale trials

Basic stress-strain tests were carried out in different temperature levels. It can be seen in Figure 13 that temperature have significant impact on stress-strain curves.

Results suggest that PET web deforms while heated and part of the deformation is due plastic strain and heat expansion. This can be seen as the total strain increases during the test (green line).

4.3 Modelling of web behaviour

Web behaviour has to be explored at least in 2 dimensions to find out possible deformations both in longitudinal and lateral directions. 2-D modelling was carried out by finite element modelling, such that the effect of heating on temperature and mechanical material behaviour were solved simultaneously.

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Modelling result and laboratory cyclic measurement for copper foil are presented in Figure 11.

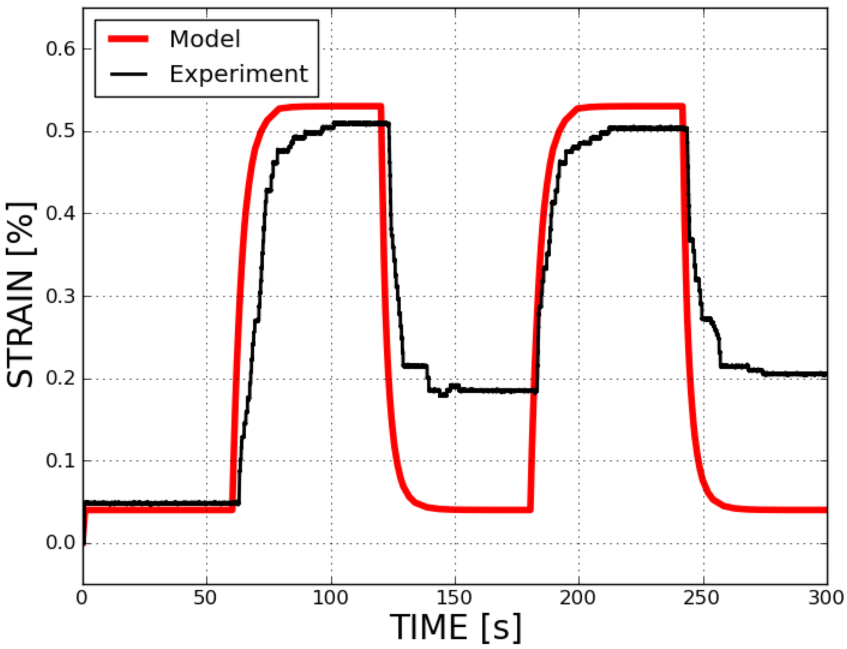

Figure 11. Modelling result and laboratory experiment in cyclic trial.

It can be seen that both methods gave approximately same strain rates when web was heated, but laboratory measurements showed some irreversible strain after heating.

Later on the printing trials of these foils were carried out in ROKO.

4.4 Discussion

Results suggest that when making batteries which are constructed/laminated of two different kinds of PET webs, one should know how the web materials responds to tension, draws and heat and further on how much they deform during the process. By material testing in various conditions it is possible to find out how different webs should be printed, e.g. what tension level, temperatures, press speeds should be chosen to get equal deformation for both webs.

Also in case of one web run the deformation can be controlled better if material behaviour is known. For example if it is known how the material deforms between printing units, one can take this information into account and vary the size of printing patterns accordingly.

Laboratory scale tests and modelling gave in many ways same results. However some crucial differences still exists and the strain mechanisms of PET foils during heating and cooling has to be studied more in detail in laboratory and in printing scale. By this way it is possible to construct a model which could be used to predict material deformations during printing process. Deformation occurring inside a printed roll has been out of scope this study, but it should be included when the web is printed several times.

The above applies even more when, as proposed by partner Imperial, a HIPE is to be printed onto one electrode, and polymerized in situ. HIPEs typically consist of two phases with radically different wetting behavior (e.g. oil/water) and therefore, “color transfer” was expected to be problematic. Another complication is that HIPEs have to be made on the printing site, since every emulsion (including HIPEs) will break with (rather) short delay after being prepared. Finally HIPEs can be cured into polyHIPEs either by thermal or UV methods.

5. Printing of separator membrane

Printing of polyHIPE membrane was studied. VTT received recipe and reagents for polyHIPE preparation from Imperial Collage.
Thermal initiator 2,2’-azobis(isobutyronitrile) and UV initiators Irgacure 819 and 184 were tested for polymerization. However, polymerisations succeed only when printed polyHIPE layer was covered with PET film prior thermal or UV treatment.

Flat screen printing was tested for printing polyHIPE membrane. 80, 165, and 200 mesh screens were used. 80 mesh (mesh opening 224 µm) screen yielded uniform layer of polyHIPE, surface was rough and mesh pattern was seen on printed surface. When using 200 mesh (mesh opening 90 µm) screen, phases began to separate.

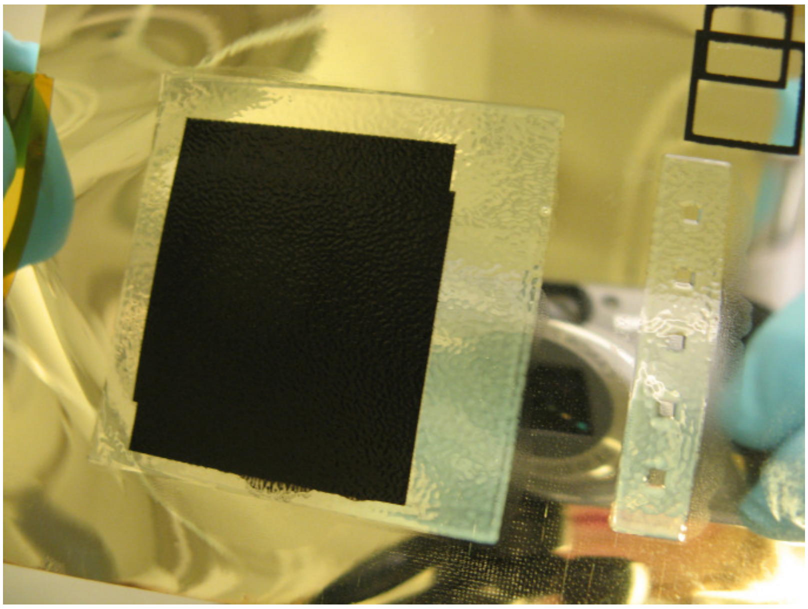

Figure 22. Screen printed polyHIPE membrane on printed cathode.

These polyHIPE printing experiments point to a possible need for very low-cost and quite small printing equipment. Small size dictated by a need to operate alongside other equipment in a chemical hood (HIPEs can be toxic) or even in a glove box. Low cost is needed because then such equipment can be procured by a number of partners in a consortium so that they can conduct and compare polyHIPE printing experiments.

A number of small experiments were carried out between NSMZ and Imperial and it was concluded that a two-tier printing structure might be useful here, where simpler printing leads to materials optimization, and the more sophisticated machines + trained personnel available e.g. at VTT would be called on at a later stage. More detail is available in the WP4 section of the Final Report.