

Development of Printed Thin and Flexible Batteries

Dipl.-Ing. (FH) Michael Wendler, Prof. Dr.-Ing. Gunter Hübner, Dr.-Ing. Martin Krebs

The paper reports from the findings of a research project named "PrintAkku" carried out in cooperation between the university of applied science "Hochschule der Medien", Stuttgart Germany and VARTA Microbattery GmbH, Ellwan-gen Germany and etifix GmbH, Grafenberg Germany. The research project is funded by the FHProfUnd program of the German Ministry of Education and Research. The screen-printing technology enables the subsequent deposition of current collector, electrode and separator/electrolyte materials onto a foil substrate in order to form a flexible filmbattery. This could be in single or multicell (series connection) layout. For the first time printed, rechargeable Ni-MH cells could be demonstrated, showing capacities of 32mAh generated by an active area of 20x20mm² and an overall thickness of about 0,6mm. The sealing issue could be solved by applying a printable, heat activated glue layer. The long-term cycling proves the stability of the cells.

1. Thin, Flexible Energy Storages

Lately there is a noticeable increase in sales of small electrical circuitry for articles of daily use. Such smart objects, stand-alone sensors, active RFIDs etc. that may be applied for "ambient intelligence" purposes will face rapid growth in future. Most of these systems will need a power supply which should be thin, flexible and adoptable to the design needs [1]. The energy capacities of those power supplies should fit to the life cycles of the applications and they should be easily disposable or recyclable. Employing printing technologies for the manufacturing of such power supplies promises cheap mass production processes, whilst keeping highest flexibility for the product designers. In the classic production processes for conventional batteries typically pick-and-place techniques are employed which require significant tooling costs for product change-over. When using printing technologies costs solely arise for new printing forms,

In this paper the focus is on electrical energy storages called batteries, distinguishing between primary (non recharge-able) and secondary (rechargeable) batteries.

Thin primary batteries using the zinc-manganese chemistry manufactured by means of printing techniques are already on the market. Such products as offered by Power Paper (www.powerpaper.com), KSW-Microtec (www.ksw-microtec.de) Thin Battery Technologies (www.thinbattery.com), Enfucell (www.enfucell.com) or a new development by ENAS Fraunhofer Institute in Chemnitz (<http://www.enas.fraunhofer.de/forschung/kompetenzen/printing-technologies/index.jsp>) presently serve niche markets (e.g., medical

anti wrinkle plaster).

The aim of the project work presented here is to manufacture secondary batteries based on Nickel Metal hydride (Ni-MH) chemistry by using the patterning techniques provided by printing processes and apply them on thin, flexible rolled plastic materials. The final goal is to bring the lab scale processes to a pre-commercial development stage by at least designing a mass production process and suitable facilities.

The idea for the work bases on the diploma thesis of B. Vindus [2], where the principal feasibility was shown. Mean-while after the preparation of several significantly improved prototypes in long-term cyclisation (recharging, discharging) tests proved the utilizability.

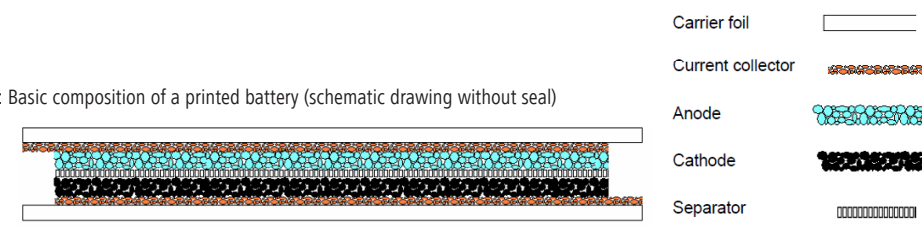
In comparison to the primary cells the secondary, rechargeable cells offer a much wider market potential. For instance smart objects or active RFID transponders equipped with such a secondary cell could have a very long life cycle. They could be recharged just by putting them onto a kind of docking station. The final application of such a printed secondary battery cell will either be a fully integrated part (e.g. printed on the same substrate as the functional – also printed -circuitry) or in the form of a self adhesive label or sticker. Especially interesting are applications in combination with photovoltaic charging assemblies.

2. Printed Batteries

The basic concept of a printed battery is shown in fig. 1. In-between two carrier foils five functional layers are embedded.

A very important role plays the separator lay-

Figure 1: Basic composition of a printed battery (schematic drawing without seal)



er. On one hand it prohibits the direct contact between the anode and the cathode layer, on the other hand the ion transport must be guaranteed throughout the whole life cycle of the cell. Therefore the separator layer is typically soaked with an electrolyte. This, however, requires that the layer is kept humid all the time. A seal against water vapor is necessary in order to avoid dehydration and complete break down of the battery.

2.1 Possible chemistry for printed batteries

Printed batteries basically use the same chemistry that is well and long known for conventional and commercially available cells. The most important types are [3], [4]:

1. Primary cells (non rechargeable)

- Zinc/Manganese-Dioxide (nominal voltage 1,5V): $\text{Zn} + 2 \text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2 \text{MnO}(\text{OH})$
- Zinc/air (nominal voltage 1,4V): $\text{Zn} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Zn}(\text{OH})_2$
- Zinc/Silver-oxide (nominal voltage 1,5V): $\text{Zn} + \text{Ag}_2\text{O} \rightarrow 2 \text{Ag} + \text{ZnO}$
- Lithium/Manganese-Dioxide (nominal voltage 3,0V): $\text{Li} + \text{MnO}_2 \rightarrow \text{MnOOLi}$

2. Secondary cells (rechargeable)

- Nickel/Metal-hydride (nominal voltage 1,2V): $\text{Metal-H} + 2 \text{NiOOH} \rightarrow \text{Metal} + 2 \text{Ni}(\text{OH})_2$
- Lithium-Ion (nominal voltage 3,7V): $\text{Li}_{1-x}\text{Mn}_2\text{O}_4 + \text{Li}_x\text{C}_n \rightarrow \text{LiMn}_2\text{O}_4 + n\text{C}$

In order to manufacture such a cell using printing technologies, all layer materials must be available as printing inks (pastes). Depending on the choice of the chemistry, however, more or less challenging problems arise. Especially the middle layer, the separator/electrolyte gave challenges. The simplest system is the Zinc-Manganese Dioxide, for which the electrolyte comprises of Zinc-Chloride. It is common to the commercially available thin film batteries that this layer is realized by deploying a fleece material which has been soaked in the liquid electrolyte and then put in place by pick-and-place techniques. This would, however, disturb a continuous sequential printing process. Thus, it would be extremely desirable to have a printable formulation of the electrolyte/separator, too. During this research work a printable paste formulation was developed.

Systems that contain Lithium are very difficult to handle. They even can be dangerous or need inert atmospheres at least. For Zinc/Air systems the air electrode is not easy to fabricate. Therefore these systems were not considered here. Whereas Zinc-Chloride is not difficult to handle the electrolytes for the Zinc/Silver and the NiMH are strongly alkaline and therefore more care has to be taken. A 25% caustic potash solution was used which after extensive experimentation, could be brought into a printable paste formulation, This formulation is currently being improved.

2.2 Detailed Design of a Printed Battery Cell

For the fabrication of a printed battery cell two basic design/layout types are practical, the stack or sandwich type and the so-called co-planar design. Fig. 2 shows the stack and fig. 3 the co-planar type. Obviously the stack type needs more layers on top of each other but has the advantage of a very short, parallel ion path that leads to much higher charge and discharge currents (peak-values).

The co-planar design has the advantage that less layers have to be printed i.e. that in principle no separator is needed, at all. The drawback, however, is that only small charge and discharge currents can be used because the spreading of the ion flux inside the electrolyte is slow having to pass across the gap between the electrodes and migrate to the very opposite ends of the electrodes.

During this research project functioning co-planar cells have been fabricated but the focus was on the stack-type which accomplished much better performance. The sequence of sketches in fig. 4 shows the step-by-step assembly of the stack type cell.

Figure 2: Stack- or Sandwich-layout of a battery cell

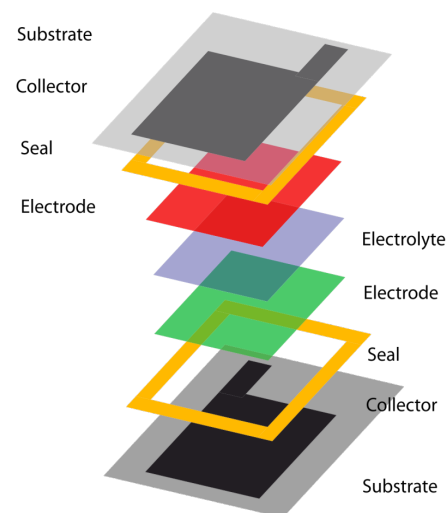


Figure 3: Co-planar or side-by-side layout of a battery cell

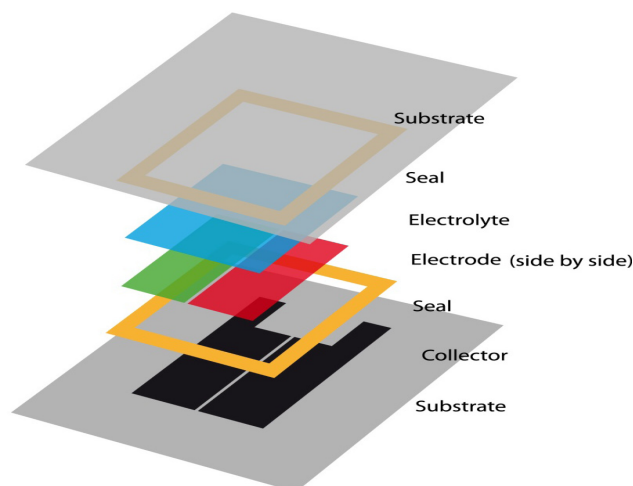
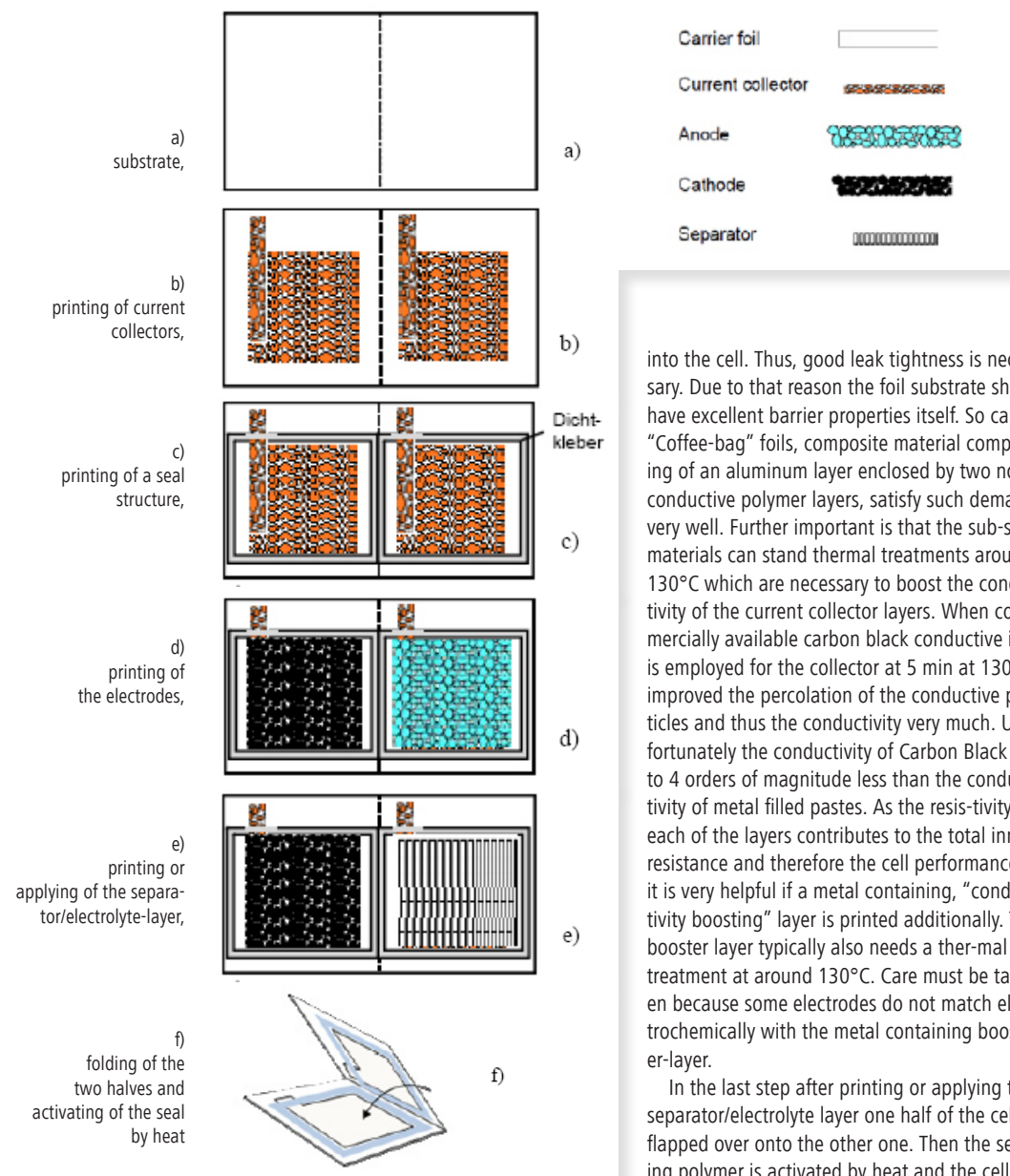


Figure 4: Sequence for assembling a stack type cell.



into the cell. Thus, good leak tightness is necessary. Due to that reason the foil substrate should have excellent barrier properties itself. So called "Coffee-bag" foils, composite material comprising of an aluminum layer enclosed by two non conductive polymer layers, satisfy such demands very well. Further important is that the sub-strate materials can stand thermal treatments around 130°C which are necessary to boost the conductivity of the current collector layers. When commercially available carbon black conductive ink is employed for the collector at 5 min at 130°C improved the percolation of the conductive particles and thus the conductivity very much. Unfortunately the conductivity of Carbon Black is 3 to 4 orders of magnitude less than the conductivity of metal filled pastes. As the resistivity of each of the layers contributes to the total inner resistance and therefore the cell performance, it is very helpful if a metal containing, "conductivity boosting" layer is printed additionally. This booster layer typically also needs a thermal treatment at around 130°C. Care must be taken because some electrodes do not match electrochemically with the metal containing booster-layer.

In the last step after printing or applying the separator/electrolyte layer one half of the cell is flapped over onto the other one. Then the sealing polymer is activated by heat and the cell thereby enclosed. Fig. 5 shows how the sealing polymer is printed around the collectors and across the collector lead-outs providing overall satisfying leak tightness.

2.2.1 Sealing (encapsulation)

As mentioned above, the inside of the cell must be kept humid during the whole life time and no CO₂ from the outside atmosphere should get

2.2.2 Electrode pastes

For conventional batteries the electrode materials are available as powders or suspensions may be called "slurries". These slurries are not suitable for printing without further treatment. First printing experiments with insufficient results are shown in fig. 6. Left hand side is the anode that exhibits inhomogeneous surface and tends to bubble. The right hand side shows the cathode with cohesive and adhesive failures.

After intensive research [5] using the DOE-methods optimized pastes for printing the electrodes could be found. The electrode particles were suspended in more than 50 different binder/solvent combinations. Due to the rather coarse particle sizes of the nickel and the metal hydride (average around 50 to 70µm) grains and the wide particle size distribution accordingly very coarse meshes for the screen printing forms had to be used where we can be sure that the particles fit through the mesh openings. From that it is evident that only screen-printing and no other printing process is able to handle such kind of materials.

Fig. 7 shows the printing results with the optimized pastes. Once the optimized formulation was found for NiMH it was rather easy to adopt the findings for the Zinc Manganese-Dioxide type. The results for the latter chemistry are shown in fig. 8.

The capacity of a printed battery is determined by the amount of electrochemically active material used. For optimum performance therefore the amount of anode and cathode material must match. Taking into account the density differences of the materials the layer thickness of the cathode should be around 2.2 times higher than the layer thickness of the anode. In screen printing it is rather easy to adjust the layer thicknesses. When printing such kind of rather large solid tone areas the mesh geometry plays the most important role whereas the influence of the stencil can be neglected. Fine-tuning of the thickness can be achieved by adjusting other printing parameters like squeegee material, pressure and edge geometry. The complete thickness of the whole printed battery including the substrates was for our prototypes around 600µm.

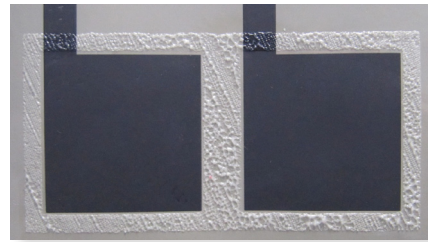


Figure 5: Current collectors with printed sealant around

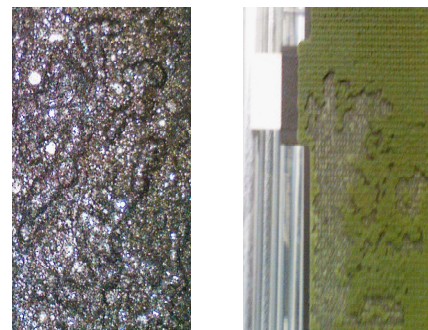


Figure 6: insufficient print quality of the electrodes

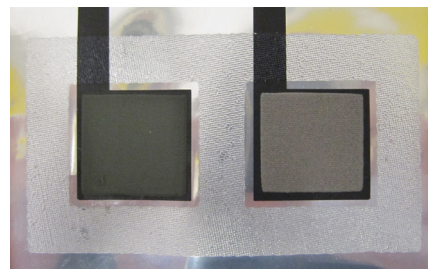


Figure 7: NiMH-Electrodes with suitable print quality, surrounded by the sealant

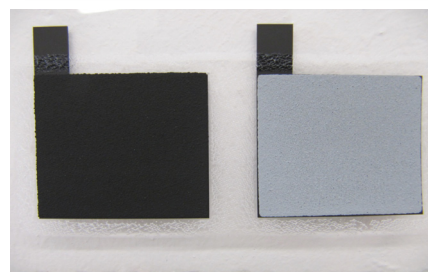


Figure 8: Zinc/Manganese-Dioxide electrodes with suitable print quality, surrounded by the sealant

3. Series Connection

The great advantages of using the printing technologies become most noticeable when designing or changing the layout which can be done in an extremely flexible way. For instance it is very easy to realize a series connection with any number of cells. Fig. 9 shows the schematic assembly

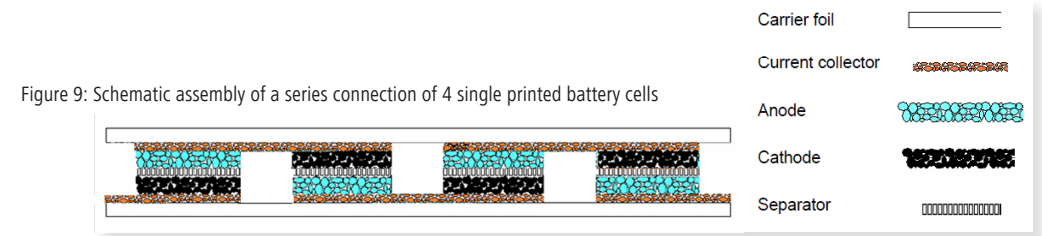


Figure 9: Schematic assembly of a series connection of 4 single printed battery cells

Figure 10: Multicell battery drives voltage converter for electroluminescent lamp

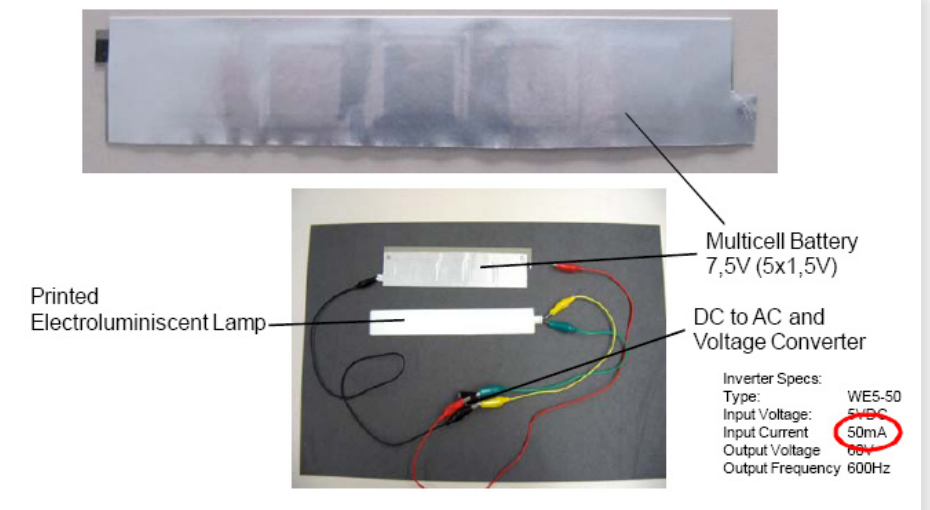
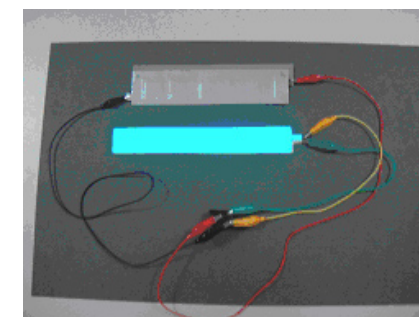


Figure 11: Multicell battery lets EL-lamp glow



assembly of four cells in a row achieving 6V output voltage (in case of zinc-manganese dioxide 1.5V x 4). For final assembly also the above shown flapping technique is used.

In fig. 10 such a multicell battery is shown which has been assembled from 5 single zinc manganese-dioxide-cells (7.5V) in a row. The output of the multicell battery is sufficient to drive a voltage converter for a (also printed) electroluminescent (EL) lamp. The converter has a nominal current intake of 50mA. The capacity of the battery was sufficient to let the lamp glow for about 15min (fig.11).

Figure 12: Cyclization of a printed NiMH cell with 1mA

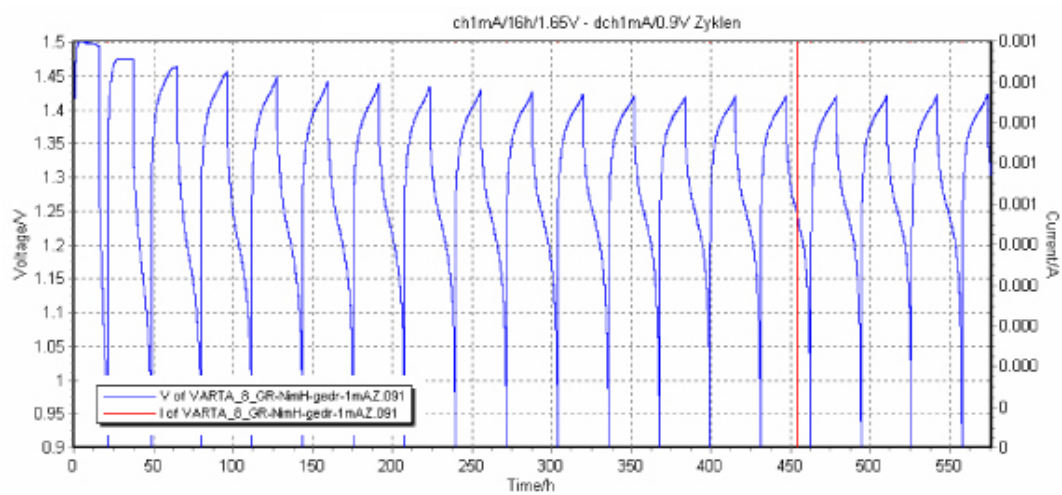
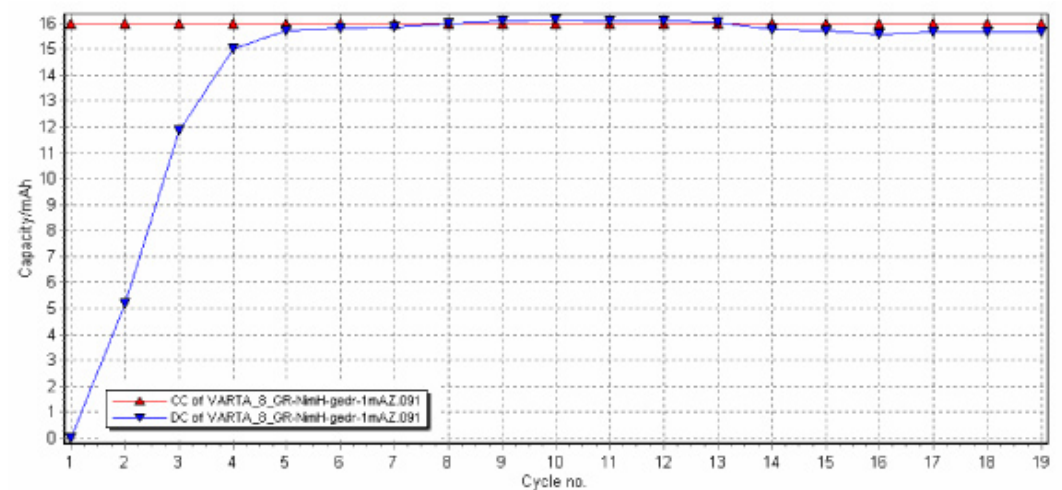


Figure 13: Capacity of a printed NiMH cell with 1mA (CC= Charge Current, DC=Discharge Current)



4. Performance tests

For the functionality of a rechargeable battery it is very important to test the long term charging and discharging performance by cyclization. Figs. 12 and 13 show the behavior of a printed rechargeable battery with an active area of 20x20mm² in such a performance test using a programmable potentiostat. According to fig. 14

the capacity is around 16mAh.

It was found that due to the lack of experience with such cells 1mA current seemed to be too low. Thus, as shown in figs. 14 and 15 during the experiment the charge and discharge current was successfully increased for one cell at the 26th cycle from 0.5 to 2mA. This cell then reached a capacity of about 32mAh.

Figure 14: Long-term cyclization of printed NiMH cells

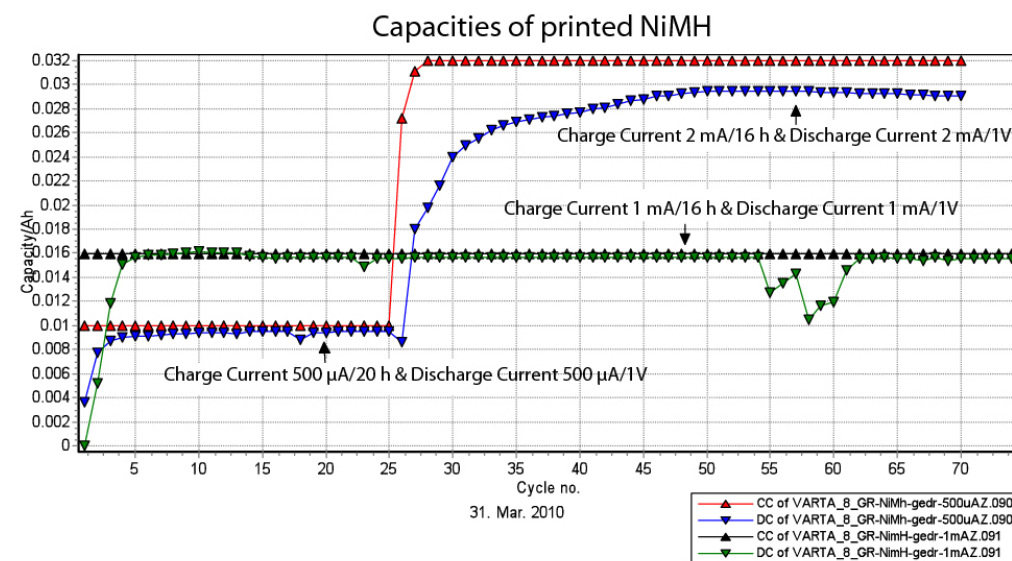
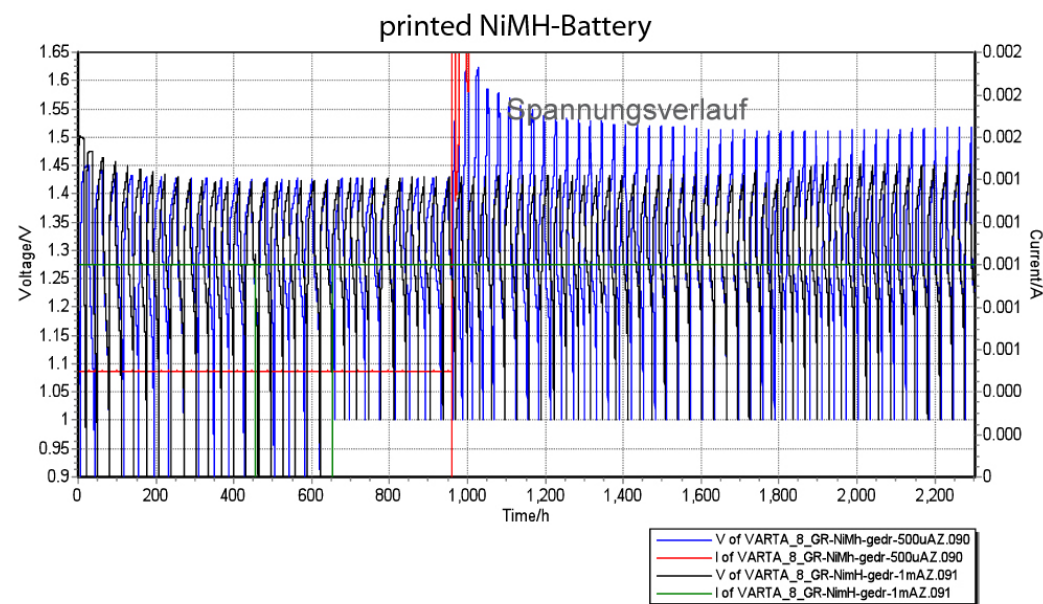


Figure 15: Capacities of printed NiMH cells during long-term cyclization. One cell is charged and discharged with 1mA, whereas for the other one the current was increased starting at the 26th cycle from 0.5 to 2mA.



5. Printed Separator

For a continuous, preferably roll to roll production process, it is very important, to use solely printing technologies, and not interrupt the production flow by assembling the separator with pick and place techniques. During this research project a method was found to bring the electrolyte, the 25% caustic potash solution into (screen-) printable form. This was done by extensive laboratory work by means of adding binder/solvent combinations and thickener agents. This electrolyte paste then also acts as separator.

Commercial print shops, in particular label printers, typically already have roll to roll printing presses equipped with at least 5 or 6 printing units. Only slight modifications have to be made regarding the intermediate drying ovens and the final folding and flapping technique, in order to be very close to start a mass production.

6. Conclusions

During the investigations presented here it could be shown that the following capacities could be achieved:

Zn MnO₂-cell (20x20mm² active material)
Charging/discharging current: 1mA
Capacity: 20mAh

NiMH-cell (20x20mm²)
Charging/discharging current: 1mA (2mA)
Capacity: 16mAh (32mAh)

In addition it could be shown that the printed batteries

- have an extremely flexible design and layout
- single and multicell batteries could be easily realized
- a printable sealing technology was developed
- a low cost production process can easily be

established

- satisfying capacities could be achieved.

At the LOPE-C trade show in Frankfurt/Main in June 2010 the printed batteries were introduced first time to the public and a concept was presented where the layout of the current collector leadouts are standardized in a way that the user can see from the position of the leadouts whether it is a primary or a secondary cell.

Further, it was suggested to increase the standard size of the active area of the battery to 40x40mm². For our cells the capacity then will increase at least calculative to about 100mAh

7. Literature

- [1] R. R. Baumann: „Printed Smart Objects: Energy and Communication Considerations“, Proceedings of Large-Area, Organic and Polymer Electronics Convention 2010 (LOPE-C 10), Frankfurt/M., June 2010, URL http://www.lope-c.com/en/conference_speakers/speaker/225/ (2010.)
- [2] [Vin2006] Vindus, Boris: „Feasibility Studie zum Drucken von NiMH-Akkumulatoren“, Diplomarbeit im Studiengang Druck- und Medientechnologie der HdM Stuttgart (10/2006).
- [3] Kiehne, Heinz Albert (5 Aufl. 2003): Batterien Grundlagen und Theorie, aktueller technischer Stand und Entwicklungstendenzen, Expert Verlag, Renningen, ISBN 3-8169-2275-9
- [4] Linden, David. Handbook of batteries. McGraw-Hill handbooks. McGraw-Hill, New York [u.a.], 2nd. ed. edition, 1995.
- [5] Hagedorn, Rico, „Optimierung einer im Siebdruck hergestellten elektrochemischen Zelle“ Bachelor Thesis im Studiengang Druck- und Medientechnologie der HdM Stuttgart 08/2009.



**Dipl.-Ing. (FH)
Michael Wendler**

Hochschule der Medien (HdM)
Institute for Applied Research (IAF)
Nobelstraße 10
70569 Stuttgart,
Germany

wendler@
hdm-stuttgart.de



**Prof. Dr.-Ing.
Gunter Hübner**

Hochschule der Medien (HdM)
Institute for Applied Research (IAF)
Nobelstraße 10
70569 Stuttgart,
Germany

huebner@
hdm-stuttgart.de



**Dr.-Ing.
Martin Krebs**

VARTA
Microbattery GmbH
R&D, Daimlerstraße 1
73479 Ellwangen,
Germany

martin.krebs@
varta-microbattery.com

(first received: 06.12.2010)