Development History and Current Achievements of Printed Primary Batteries

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Abstract

Since the end of the last century tremendous efforts have been spent to utilize various aspects of printed electronics' components. One aspect in driving electronics is to provide electrical energy for it. The most appropriate way is to employ printing approaches rather than assembly processes for the integration of battery technology. Doing so, the application basically can be fully printed – if all components are printable.

Looking for commercial applications, there are already some available on the market: e.g. temperature logger, RFID smart tagging cards, or cosmetic patches.

In this paper a review on printed primary batteries is presented and discussed. Since 2007 Fraunhofer ENAS and Chemnitz University of Technology are active in developing and manufacturing printed batteries and applications thereof. Besides the historical sketch also the current achievements are shown and discussed.

Introduction

Battery technology is evident for more than a century. Especially mobile applications demand portable electrical power solutions. The range of applications is tremendous, just to enumerate a few: cars, engines, mobile phones, notebooks, radios, flash lights, clocks, watches, hearing aids, or even pacemakers. Due to the manifold of applications many casing of batteries have been standardized. Looking at the drugstore one will find the well-known AA, AAA, C, or D cell or also coin batteries which are metal encapsulated. This standardization has the advantage that a designer of a new device can choose from a bunch of existing form factors and energy contents. The drawback is that new devices need to be designed according to existing batteries.

Looking at technical equipment (e.g. cameras, smart phones, tablets, or notebooks) this approach changed dramatically. Nearly every model has its own battery design. This shows the big impact that is caused by the strategy which part is first: battery or device design. [1-4]

In printed battery business both approaches can be found. A number of standardized batteries are offered at the market. In these cases any user can take the existing battery design and make his application matching the available performance characteristics. This includes sometimes a lack or a surplus of energy content – therefore, a malfunction of the application or a waste of energy. The second approach is to scale the performance characteristics of the battery according to the demands of the application. This freedom is enabled by the approach of printed batteries in general.

Besides these aspects there is a fundamental difference in battery technologies: primary and secondary batteries. Primary batteries are containing a defined energy content after manufacturing and can be used as they are. When they become empty they have to be recycled. Typical applications driven by primary batteries are watches, flash lamps, or radios. Contrary to primary batteries, secondary batteries can be recharged several times. After production they need some conditioning cycles to become fully activated. Attention must be paid to not overcharge nor exhausted because this both charge conditions will damage the battery and possibly the device or user.

Looking at the particularly involved material systems and the technology required, it turns out that primary batteries can be much easier and user-friendly used in low-cost and time-limited applications than secondary batteries for two aspects. Firstly, primary batteries can be realized by only harmless and mild ingredients that cannot harm anybody. Basically, it can be called "green" in contrast to aggressive and hazard alkaline chemicals of secondary batteries. Secondly, primary batteries do not require any activation nor recharge cycle and therefore do not need any connection or electrical circuit for this purpose to the outside world. In this respect primary batteries can be fully integrated into the application.

Comparing different primary battery systems (ref. Fig. 1) zinc chloride has one of the lowest energy densities.

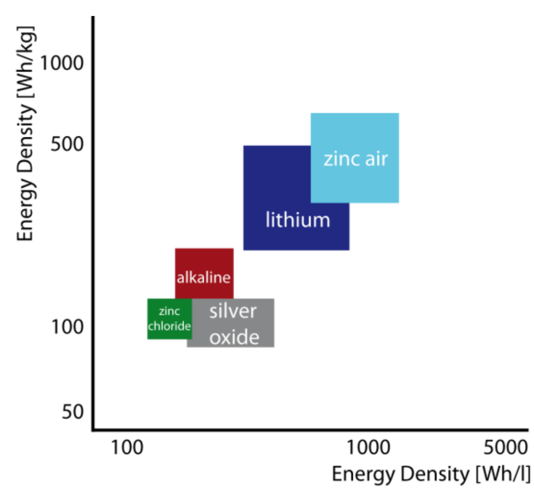

Figure 1: Comparison of the energy storage capability of various primary battery systems. (rework from [5])

Nevertheless, carbon zinc is very attractive for applications in printed electronics. Fig. 2 gives an overview about common primary battery technologies and mention the related material system for anode, electrolyte, and cathode, respectively. When comparing the electrolyte materials it is evident that the only 'green' is zinc chloride.

	zinc-carbon: zinc chloride	zinc-carbon: alkaline	lithium	silver oxide	zinc air
anode	zinc	zinc	lithium	zinc	zinc
electrolyte	zinc chloride	alkaline (KOH/NaOH)	salt of lithium	alkaline (KOH/NaOH)	alkaline (KOH/NaOH)
cathode	MnO_2	MnO_2	MnO_2	silver oxide	metal catalyst

Figure 2. Some of well-established primary battery concepts and their basic chemicals for anode, electrolyte, and cathode © Fraunhofer ENAS

Looking at the market, for most low cost applications batteries of the zinc chloride type are employed. Using this chemical system there is no need for any recharge making any application development much simpler.

Printed Batteries in Published Literature

Literature research via Scopus for "printed batteries" delivers only a very few results (in the order of 15) in the time regime 2006 – 2017. Analyzing the results most matches do not coincide with the intention but combine some printing efforts with any kind of non-printed battery for energy deliverance. Nevertheless, there have been recently some very comprehensive review papers dealing with the topic of printed batteries [1,6].

For our activities we experienced a tremendous media response back in 2009 stating with a small notice in the exhibition newsletter of the Nanotech Exhibition in Tokyo, Japan. In the same year the New York Times Magazine awarded our printed batteries in the section Technology in the 9th annual year of ideas. [7]

Commercial companies have not published their results on conferences but on exhibitions and showcases.

Printed Primary Batteries

Layout

Every printed battery consists of a substrate (polymeric film or metal foil), a current collector (carbon plus metal layer if necessary), an anode (zinc), a cathode (manganese dioxide), an electrolyte (zinc chloride based), and for a stacked layout a separator layer (mechanical distance between anode and cathode). A layout of such setup is given in Fig. 3.

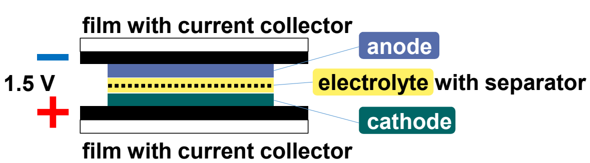

Figure 3. Layout of a printed battery setup © Fraunhofer ENAS

Each component has a dedicated functionality:

- The substrate is the carrier for all layers and also used as encapsulation material.
- The current collectors interconnect the terminals of the battery with the electrode (anode and cathode) materials to conduct the electrons and close the circuit. If they are simply made out of carbon they can be easily scratched.
- The anode delivers electrons in an oxidation process.
- The cathode collects electrons in a reduction process.
- The electrolyte enables ionic movement between cathode and anode inside the battery to close the circuit.
- The separator is necessary to prohibit any short circuit between anode and cathode inside the battery cell. The separator layer can be omitted if the electrode areas are located and separated from each other side-by-side.

Manufacturing Process

Screen Printing Technology

In a printed battery materials for current collectors, anode, cathode, electrolyte, and encapsulation are used in form of an ink to deposit each layer onto a substrate. Due to grainy ingredients and typical layer thicknesses in the range of 10 to 40 µm there are only two established deposition technologies suitable: screen printing and coating. Screen printing (see Fig. 4) is working pattern wise while coating can only generate stripes of finite lengths. Both technologies have advantages and disadvantages. Based on the fact that printed batteries need not to be rectangular in shape, screen printing is the preferred choice.

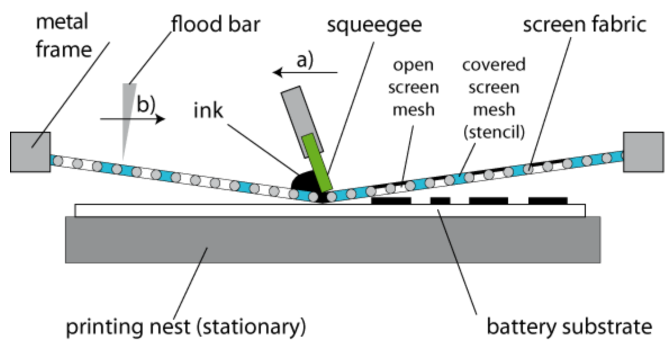

Figure 4. Setup of a flatbed screen printer (explanation see text) © Fraunhofer ENAS

In the screen printing process the substrate is fixed to a printing nest, in most cases by gluing or by vacuum. The intended printing pattern has been transferred into the stencil of a printing screen (blue) which itself is fixed to a metal frame for generating the necessary screen tension. All non-covered mesh pores are still open and can transfer ink from the upside to the downside of the screen. For the printing step the ink is deposited on the top side of the screen and moved by a squeegee in process step a). The squeegee itself causes a defined pressure onto the screen so that there is only one line of contact between screen and substrate in which ink is transferred and deposited onto the substrate. Having reached the left end of the screen the squeegee is lifted up and a metal flood bar moves in process step b) the remaining ink back to the starting position and distributes some ink across the screen. In this process step there is no contact between screen and substrate.

Production steps of batteries

Employing screen printing each layer is printed separately and dried after deposition. This is true for the current collector, anode and cathode.

In the next step an adhesive layer for encapsulation is printed around the pattern of the active battery layers. This layer will be used for sealing the battery in a later process step.

For prohibiting a direct contact between the two electrodes a separator layer is necessary. There are different approaches used: a) an additional layer consisting of a porous paper or membrane. b) spacers like polymer or glass spheres in the electrolyte ink. c) printed patterns of an adequate height and distance.

The electrolyte can then be printed on one or both electrodes and need to stay wet for a proper functionality of the battery.

As the last lamination step for the battery the anode and cathode side need to be attached and sealed.

Features

Printed Batteries are electrochemical energy systems. The terminal voltage is determined by the reacting chemicals. For a zinc manganese system this is about 1.5 V_{nom}. This voltage is called nominal voltage [V_{nom}]. Measuring the voltage at the terminal contacts will give between 0 V (faulty battery) and 1.6 V (fresh battery) – dependent on the charge and discharge conditions of the battery. This voltage is called 'closed circuit voltage' [V_{CCV}].

Each battery has an internal electrical resistance R_i. This internal resistance limits the current that can be drawn from the battery. The resistance summarizes resistance of the current collectors and the ease of ionic movement inside the battery cell. The ionic movement is slowed down when further discharge of the battery happens. As the result R_i will increase when the battery is discharged.

The charge of a printed battery scales with the area size of active electrode material. Therefore, a usual way of counting the charge of a printed battery is to give the area capacity [mAh/cm²]. A usual value is 2 … 5 mAh/cm². If the active area is 4 cm² the battery has a capacity of 8 … 20 mAh.

Upscaling Voltage

The usual approach to scale voltages to multiples of 1.5 V_{nom} is a series connection of single battery cells.

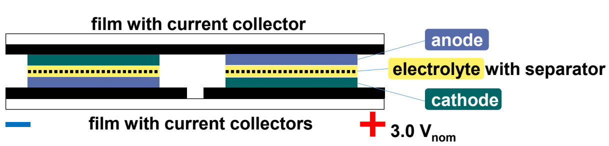

Figure 5. Layout of a series connection of two printed batteries © Fraunhofer ENAS

In Fig. 5 the layout of two batteries supplying 3 V_{nom} in series connection is given. The interconnection is simply done by using the same current collector on the upper substrate. In the printing design anode and cathode needs to be reversed for both batteries.

Based on this approach batteries up to +/- 15 V_{nom} have been demonstrated. (see Fig. 10) [8]

When scaling up voltage one have to take into account that the total battery size scales with the number of single cells. Although the area capacity is e.g. 4 mAh/cm² for a single 1.5 V_{nom} cell, a 3.0 V_{nom} cell will need the double size and therefore the area capacity will scale down to 2 mAh/cm².

Upscaling Current

One important factor for the overall internal resistance R_i of a battery is the current collector. This layer consists of carbon. To decrease R_i a beneath silver layer can be used. For cost efficiency reasons this can be done as a grid (see Fig. 7).

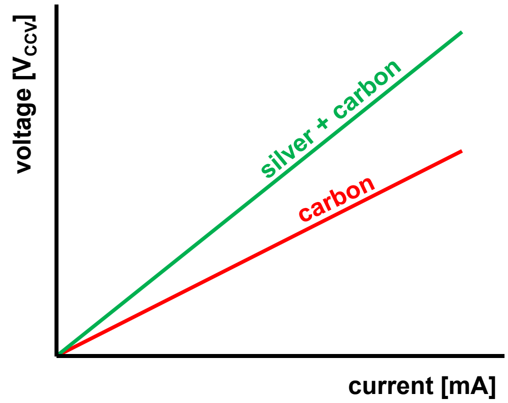

Figure 6. Closed circuit voltage in dependence of the load for batteries with different current collectors © Fraunhofer ENAS

Figure 7. Printed batteries up) with and down) without silver grid. The upper battery contains three cells, the lower four. © Fraunhofer ENAS

Improving Battery Performance

The most important parameter of a printed battery is the internal resistance R_i. By improving the layout pattern (broaden current collectors) or adding a patterned silver layer (see above), R_i can be dramatically lowered.

The other way to lower R_i is the appropriate internal setup of the battery. An unsuitable separator layer of the battery constrains the ionic movement and therefore increases R_i.

The materials employed for building the battery have a dramatic effect on the battery performance. Choosing appropriate carbon, zinc, and manganese dioxide chemicals and fine-tuning the ink formulations can tweak the overall performance.

Tailoring of Batteries

The most important feature of printed batteries is that they can be adjusted to drive the intended application. This is usually done according to

- Voltage
- Capacity
- Min./max. current
- Lifetime
- Size
- Application shape

Some of these parameters are dependent: e.g. a higher capacity or a higher voltage require a bigger size. As examples the capacity/size as well as the application shape are discussed.

Scaling of Area Size

The capacity of batteries directly scales with their geometrical size of the active electrodes as shown in Fig. 8.

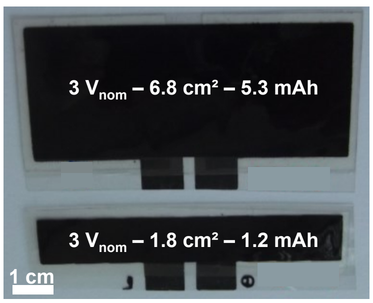

Figure 8. Two batteries of 3 V_{nom} with different sizes. The capacity scales with the size of the active areas. © Fraunhofer ENAS

Matching of Application Shape

Printed batteries are predestinated for matching the shape of an application. In Fig. 8 an example is given.

Variety of Substrates

Printed batteries are usually known to use flexible substrates that are polymeric films (e.g. PET, PEN, PI, PC) or coated aluminum. Furthermore, it has been proven that also coated paper or even technical textiles can be employed. Therefore, as long as the water content of the electrolyte stays inside the cell a wide variety of substrates can be used.

Applications Driven by Printed Batteries

The charm of printed batteries is to drive flexible printed applications and in this approach enable a manufacturing chain solely based on printing technologies. The big advantage compared to assembled applications is that all interconnects are realized by printing technologies. In this way no interconnection issues will arise.

Advertisement

One basic application for printed batteries is to deliver electrical energy to portable advertisement products like greeting cards. The obstacle for this application is still the bad availability of printed OLEDs. Therefore, in most cases ordinary SMD LEDs are used as illumination element.

Figure 9. Inlay of a greeting card, driving an orange LED by two curved batteries. The printed push button is pressed by a pencil. © Fraunhofer ENAS

Sensor Device

Standalone portable sensor devices also usually require electrical energy. One approach is to have a base station and simply exchange the sensor itself. This is well known in case of home testing of glucose levels.

When integrating everything into one flexible device then also the energy storage has to be integrated into the device. In this scenario a printed battery is an appropriate solution. In 2013 the OE-A awarded project results of SIMS (FP 7, GA 257372) as best publically funded project demonstrator. In this demonstrator the integration of printed devices (a EC display, a sensor and a battery) was proven. [9]

For this project also a +/15 V_{nom} battery has been designed (see Fig. 10). While the - 15 V_{nom} channel required a load of 200 µA the + 15 V_{nom} channel required a load of just 10 µA. In the battery design lower current only require smaller patterns.

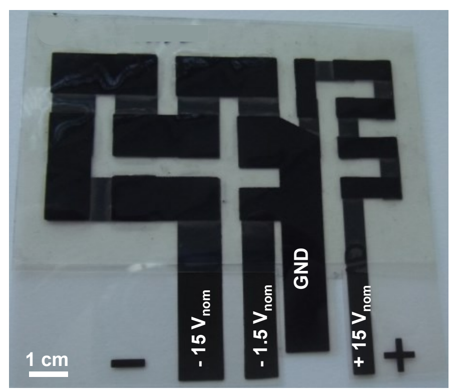

Figure 10. Printed +/- 15 V_{nom} battery for driving different currents © Fraunhofer ENAS

Commercially available applications

The most prominent commercial application driven by printed batteries is a temperature logger for the human body called TempTrack® [10] In this plaster a Bluetooth low energy (BLE) setup is used to record and transmit the skin temperature of a person. The intention is to track the body temperature of a baby without disturbing it in sleep. The energy last for about 24 h.

Other applications commercially available are e.g. temperature logger, RFID smart tagging cards, or cosmetic patches.

Conclusions and Outlook

Printed batteries have shown a big development over the last two decades. Starting with single battery elements meanwhile commercial applications are available. The chemical ingredients are still the original ones while the preparation and manufacturing has changed a lot.

Printed primary batteries have a well-defined operational range for applications. The adjustment of energy content can be done very accurately so that little amounts of energy get wasted. The materials used are non-toxic.

Looking into the future printed batteries will drive applications of the Internet of Things (IoT). Energy concepts are under development to save energy in electronics by sleep mode states. Several market studies expect that printed electronics will have an important impact of IoT elements and a printed battery perfectly matches these developments.

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Author Biography

Andreas Willert received his Diploma in physics from Christian-Albrechts-Universität in Kiel, Germany (1995) and his PhD in physics from Chemnitz University of Technology, Germany (2000). Since 2003 he has worked on the application of printing technologies. Since 2007 his focus is on the application of functional material employing printing technologies on various kinds of substrates and the annealing / sintering thereof. He is project manager and develops hybrid applications including printed battery systems.