http://dx.doi.org/10.5755/j01.eee.20.8.8434 ELEKTRONIKA IR ELEKTROTECHNIKA, ISSN 1392-1215, VOL. 20, NO. 9, 2014

Monometallic Textile Electrodes for “Green” Batteries

L. Vojtech[1], J. Hajek[1], M. Neruda[1], M. Zatloukal[2]
[1]*Department of Telecommunication Engineering, Czech Technical University in Prague, Technicka 2, 16627, Prague, Czech Republic*
[2]*Centre for Research and Utilization of Renewable Energy Sources, Brno University of Technology, Technicka 3058/10, 61600, Brno, Czech Republic*
lukas.vojtech@fel.cvut.cz

Abstract—**Global trends in the development of modern electrical devices include also eco-friendly demands. One of the areas is seen in environmentally friendly batteries (electrochemical power sources) which do not contain poisonous and heavy metals. Modern structures based on coated textile materials are an alternative to the current all-metal electrodes. The use of environmentally friendly metals often entails the necessity to apply multiple layers of metals, which negatively affects the lifetime of the electrodes and battery cells. Accordingly, this paper focuses on the design and manufacture of monometallic textile electrodes for "green" batteries, i.e. the use of ecological technologies for eco-friendly electronics, especially the new-generation electrochemical power sources. The proposed technological processes were verified by realization of specimens and measurement in laboratory conditions with good results. Industrially applicable technologies were used for applying a thick monometallic deposit to create the specimens. This will allow future mass production and deployment in electrical engineering applications.**

Index Terms—**Batteries, electrochemical devices, electrodes, textiles.**

I. INTRODUCTION

Modern trends in the development of new and rapidly applicable electrical engineering technology have become increasingly focused on environmentally friendly elements. The result is a new "green" electrical engineering which the EU expects to put in practice by 2020 under the Horizon 2020 framework program [1]. The goals of this program include practical application of modern organic components and circuit structures and also environmentally friendly (hence "green") electrochemical sources [2]. A survey of the current situation in the development of electrode and battery separators reveals new types of textile fibers (e.g. linear fabrics) as a promising area of development [3]. Planar electrically conductive fabrics have been used for many years in protective clothing to distribute the electric charge evenly on the fabric surface. With a proper conductive structure, i.e. if the desired electrical conductivity is obtained, such materials ensure protection against ESD (electrostatic discharge) [4]. Recent years have witnessed advances in increasing the electrical conductivity of materials while the application focus shifted to the implementation of flexible electrically conductive elements or electromagnetic shielding [5]. Considering the substantial surface area exhibited by textile materials due to their structure and the fibers used, it may be expedient to use these materials as electrode carriers with a maximum surface area, as is necessary for the manufacture of electrochemical cells – batteries. Such applications have been described in literature, particularly the creation of supercapacitors based on nanotextiles, i.e. textiles with a fiber diameter not greater than 100^{-9} m [6].

II. EXPERIMENTAL PRODUCTION OF ELECTRODES FOR GREEN BATTERIES

A basic requirement for newly developed electrode materials is their readiness for mass production. This aspect shall be taken into account already during the research and development of the electrodes and the technological processes for their manufacture. Other considerations that need to be taken into account include keeping the required chemical resistance of the electrodes, a maximum effective area at minimum dimensions, and the weight of the electrodes.

The requirement for maximum efficiency of battery cells drives the search for material structures with a maximum surface area. Nanotextiles thus appear to be an ideal electrode carrier, as the originally nonconductive fiber can be coated with the desired electrode metal. Currently, nanotextiles can be manufactured from polymers of specified chemical resistance properties, for example ELMARCO [7] nanotextiles, which are commercially available.

These nanotextiles cannot be combined with strongly alkaline electrolytes because they are made of PVDF (polyvinylidene difluoride), PVDF copolymers and PAN (polyacrylonitrile) [7], and as such are not resistant to 6M KOH electrolytes [8]. The development of new types of environmentally friendly electrochemical power sources must rely on eco-friendly metals (zinc, tin, copper) and strong alkaline electrolytes in the form of gel [9].

PP (Polypropylene), in particular, is highly resistant

Manuscript received January 27, 2014; accepted May 25, 2014.
This research was funded by a grant Kompozitex (No. FR–TI4/202) from the Ministry of Industry and Trade and grant Center for Research and Utilization of Renewable Energy (No. CZ.1.05/2.1.00/01.0014) from the Research and Development for Innovations Operational Programme.

against strong alkaline and acidic chemicals. PP is widely used in chemical technologies and components. PP fiber-based textiles first need to be made conductive before they can be used as an electrode.

This can be done by several techniques:

- Metal powder coating;
- Physical methods of coating in vacuum;
- Chemical coating;
- Electroplating.

III. REQUIREMENTS ON ELECTRODES AND THEIR PERFORMANCE

Sufficiently conductive "green" electrodes with a current carrying capacity for use in battery cells must meet the following characteristics, the attainment of which was the primary objective of the present research.

A. Chemical Resistance of the Substrate

This requirement is met by the use of textile materials based on PP, which can resist the desired 6M KOH solution in a long term.

B. Maximum Substrate Surface Area

Among textile fabric technologies, PP nonwoven fabrics seem to be the ideal choice, because they exhibit a higher surface area compared to woven fabrics while having the same fabric density. A maximum resulting surface area to weight ratio can be achieved by an analysis of electrodes applied on mechanically reinforced substrates (needling or weaving fibers among layers) or heat reinforced substrates (sintering fibers into isles).

Chemical hardening is not a practical solution, as it could become a source of technological difficulties due to chemical pollution affecting both the manufacturing bath and the cells themselves.

C. Conductive Electrode Layer Material

Nickel, which is being phased out in the consumer industry for environmental reasons, and tin, which is environmentally friendly and non-allergenic, appears to be the best choices for strongly alkaline electrolytes. The formation of undesirable bimetals or intermetallic products caused by the deposition of metal layers containing only one metal must be avoided. This means that a monometallic electrode is to be preferred.

D. Electrical Load of the Metal Layer

Thicknesses in the order of tens of µm are considered, especially due to the current demands on battery charging and operation and also in order to avoid loss of the electrode metal caused by primary spontaneous dissolution.

E. Depth Profile of the Metal Layer

Maximizing the surface area of the working part of the electrode is related not only to the fabric surface, but also to the internal volume. It is assumed that the individual coated fibers of the fabric will be in contact with the battery electrolyte in the greatest possible depth profile. Consequently, our goal would be a coating with a maximum throwing power.

IV. TECHNOLOGY PREPARATION OF MONOMETALLIC LAYERS

The analysis of the above-mentioned requirements and available technologies reveals that the required properties of the described procedures cannot be obtained. The solution, however, lies in a combination of several procedures. The experiment would entail a deposition of tin metal, because tin is a "greener" metal than nickel. The research is therefore primarily focused on a new type of alkaline battery cells based on this eco-friendly metal.

A. Fabric Pretreatment

The fabric needs to be washed or degreased first, as pretreatments on the basis of synthetic and organic chemicals are commonly used in the textile industry. The starch that remains after the textile is pretreated could affect the deposition of electroformed layers (e.g. internal stress of metals or formation of amorphous layers). Grease residues impair the quality of the vapor-deposited tin metal layers.

The washing of the base material takes 15 minutes in a bath heated to 70 °C. The bath contains 1.5 % NaOH solution in DI water. The washing procedure is followed by rinsing the material in DI water for 10 minutes and drying it with hot air.

B. Sample Preparation

The sample is placed onto a frame that supplies the electrical power and ensures the proper suspension and attachment of the textile sample. The frame is made of 2.5 mm^2 copper wire. Fig. 1 shows the preparation of the sample after the vacuum deposition of tin.

C. Vacuum Deposition

A sufficiently thick layer must be deposited on either one or both sides of the sample depending on the requirements on the sample electrode, Fig. 1. The metal evaporation tray should be full to ensure that an adequate layer of tin is deposited. This reduces spontaneous dissolution during the subsequent electroforming reinforcement of the layer.

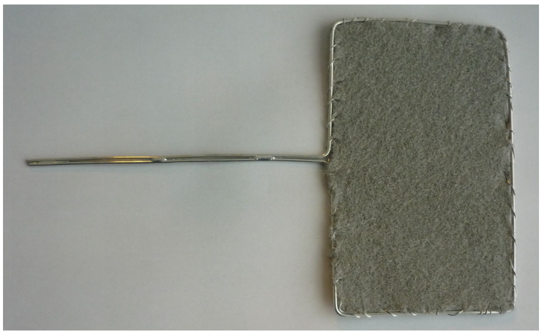

Fig. 1. Sample of PP textile – vacuum tin coating.

D. Electroforming – Reinforcement of the Tin Layer

The electroformed tin metal layer, which reinforces the initial vapor-deposited tin film, is applied in an alkaline tinning bath, since the electrode will be operated in an alkaline environment. Furthermore, alkaline tinning baths have higher throwing power. Although the alkaline (battery cell) electrolyte will be based on KOH, a tinning bath with NaOH may be used. Both baths are prepared with Na_2SnO_3

or K_2SnO_3 and the appropriate hydroxide.

According to [10], the tinning bath consists of Na_2SnO_3 at a concentration of 105 g/l and 10 g/l NaOH in DI water. The normal anode/cathode area ratio is 1:1. The bath should be operated at a temperature of 70 °C.

The initial coating requires the placement of a plated electrode in a bath with a current density $J_{\text{plating}} = 1$ A/dm2. The duration of the initial coating is $t_{\text{plating}} = 15$ min.

The initial coating is followed by the first reinforcement of the layer at a current density $J_{\text{reinforcement1}} = 5$ A/dm2 for t = 55 min.

Different conditions characterize the second reinforcement, i.e. current density $\mathrm{J}_{\text{reinforcement2}} = 20$ A/dm2, t = 30 min. Tin anodes are not covered with the standard yellow and green layer indicating the anode polarization. Under the operating conditions described above these would turn dark grey and tin would be released to the bath in the form of divalent ions, resulting in a tough coating with a higher surface area compared to conventional decorative gloss paints based on tetravalent ions [4]. The main reason for this is the smaller surface area of the anode compared to the cathode. Another effect is the generation of considerable amounts of oxygen in the electrolyte.

After the layers have been deposited, the sample is rinsed with DI water over the bath and washed under running water to remove the bath residues from the fabric. Then it's dried.

After carefully drying the sample, the suspensions are removed with lever shears. The textile monometallic sample electrode is ready.

V. DISCUSSIONS

The proposed technological processes were verified in laboratory conditions with good results. Figure 2–Fig. 5 depict macro pictures of realized electrodes. Moreover, the electroforming procedures made it possible to coat the extending fibers not only from the front toward the anode, but also on the sides, which is impossible in most electrolytes due to depth efficiency. On average, 0.72 g/cm^2 of tin was deposited on a unilateral electrode. Cyclic stress-strain tests of the conductive felt structure (3D structure) as a collector and carrier of electrode materials in an alkaline battery showed good results and stability of the deposited monometallic layer. The main criteria for the evaluation of the collector included the generation of hydrogen under cyclic stress (charging and discharging of a battery), successful application of an active material to the collector, and ultimately, comparison with other materials – nets, pocket electrodes etc.

Fig. 2. Monometallic tin felt electrode ready for filling (non-woven PP textile carrier prepared by needling).

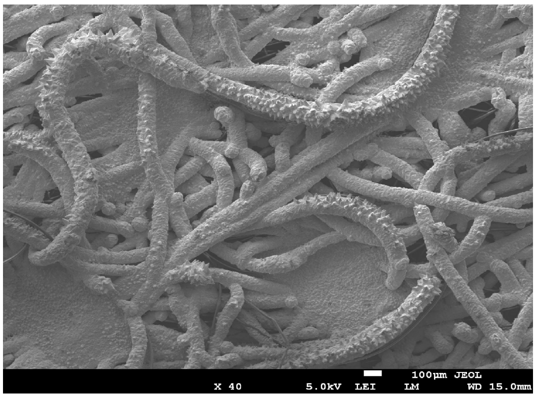

Fig. 3. Monometallic tin electrode on needled PP.

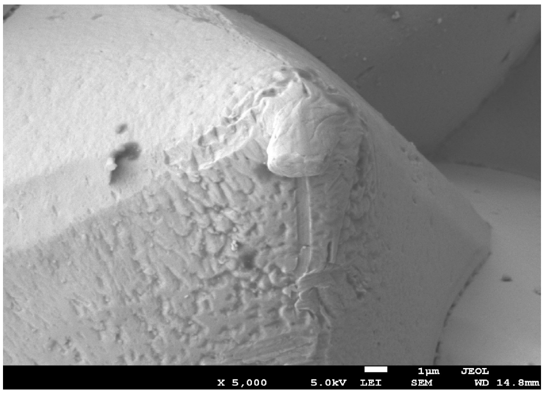

Fig. 4. Detail of the crystal surface of divalent tin in a monometallic tin electrode.

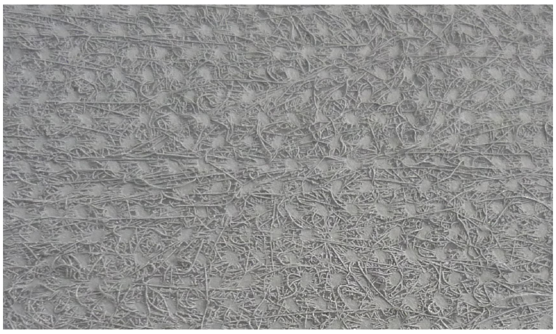

Fig. 5. Macro picture of a monometallic tin electrode on heat reinforced PP.

VI. MEASUREMENT RESULTS

Several methods may be used for measuring the effective surface area of the electrodes. The methods are usually based on optical (3D surface measurement) or electrochemical (electrical conductivity) principles. One of the optical methods is a surface area calculation based on processing scanned images at different angles [11]. However, low frequency conductometry is utilized more frequently [12]. This method is based on measuring the electrolyte conductance G between the two electrodes of the surface area A and the distance l between them. This method can be used either to measure the surface area of the electrodes using a calibrated and analyzed electrode, or for comparative measurements. Comparative measurements were used also in the present research. All electrodes were set in an electrolysis beaker with water and resistance was measured under stable conditions described below, Fig. 6.

The following conditions were used for comparative measurements:

– All-metal copper board electrodes were used for comparative measurements. These electrodes were galvanized with tin metal in the same type of galvanic bath as the thick layers deposited onto the textile electrodes.

– The same type of electrolyte (i.e. DI water with a conductance of 15 µS) and the same temperature of 20 °C were used.

– The same geometry of the test cell, electrode distance and dimensions of the electrodes were used.

– Measurement of resistance (conductance) between electrodes was performed with a measurement signal at the frequency of 100 Hz.

Fig. 6. Assembly for electrodes measurement.

While maintaining these conditions, conductance can be calculated as follows

$$G = \frac{1}{R} = \copyright \cdot \frac{A}{l}, \tag{1}$$

where G specifies conductance [S], R denotes resistance [Ω], κ represents electric conductivity [$\mathrm{S.cm^{-1}}$], A specifies the surface area of the electrodes [$\mathrm{cm^2}$] and l denotes the distance between the electrodes [cm].

TABLE I. MEASUREMENT RESULTS.

Base material of electrodes	Resistance of specific electrode	Value	Unit
Cu//Sn	$R_{\mathrm{Cu//Sn}}$	9.12	kΩ
Needled PP//Sn	$R_{\mathrm{Needled\ PP//Sn}}$	9.53	kΩ
Heat reinforced PP//Sn	$R_{\mathrm{Heat\ reinforced\ PP//Sn}}$	9.03	kΩ

Table I depicts measurement results for three different base materials of electrodes. Electrode $R_{\mathrm{Heat\ reinforced\ PP//Sn}}$ reaches the lowest resistance value, i.e. biggest specific conductance value and a greater effective surface area as shown in (1) in comparison with the reference all-metal electrode $R_{\mathrm{Cu//Sn}}$. The biggest resistance value, i.e. lowest specific conductance value and effective surface area, is observed at the electrode $R_{\mathrm{Needled\ PP//Sn}}$.

VII. CONCLUSIONS

The goal of the research project was to design and experimentally validate a technology for the preparation of monometallic layers of tin with a maximum surface area deposited on a PP textile substrate, with the intended application in “green” electrodes in electrochemical power sources. The paper describes several procedures and presents the results confirming the project goals. The proposed technologies allow mass manufacturing. During the work on this paper, a promising path for continued research in this area has been identified. Laboratory tests were carried out on unilaterally or bilaterally coated samples on various types of PP substrates, different reinforced fabrics, and at different planar densities. The samples also passed laboratory tests for cyclic stress-strain resistance in a measuring cell of an electrochemical cell between cycles of charging and discharging. A comparison of the observed values of conductance in the experimental measuring cell shows that the electrode $R_{\mathrm{Heat\ reinforced\ PP//Sn}}$ has a greater effective surface area than the reference all-metal electrode $R_{\mathrm{Cu//Sn}}$, while $R_{\mathrm{Needled\ PP//Sn}}$ has a smaller effective surface area than the reference electrode. The most important feature of the proposed textile electrodes is the ability to absorb liquid electrolyte or electrode paste, if implemented in a battery cell. The electrode $R_{\mathrm{Needled\ PP//Sn}}$ seems more advantageous in this perspective, as its material has the maximum electrolyte absorption capacity at the expense of a less efficient surface area. Still, textile electrodes lead to improvements in the battery capacity/weight ratio.

Future research may focus on the application of orthogonal nanostructures on the initially coated fibers of the PP textile. The technology of nano-bar deposition appears to be a promising substitute of chemically deposited nanotubes in order to obtain a strong current-stressed layer.

REFERENCES

[1] *Green Paper - From Challenges to Opportunities: Towards a Common Strategic Framework for EU Research and Innovation funding*, Horizon 2020, 2011. [Online]. Available: http://ec.europa.eu/research/horizon2020/pdf/com_2011_0048_csf_green_paper_en.pdf#page=2

[2] *Towards Green Electronics in Europe: Strategic Research Agenda Organic & Large Area Electronics*, CORDIS of European Commission, 2009. [Online]. Available: http://cordis.europa.eu/fp7/ict/photonics/docs/reports/olae-sra_en.pdf.

[3] L. Ji, X. Zhang, “Fabrication of porous carbon/Si composite nanofibers as high-capacity battery electrodes”, *Electrochemistry Communications*, vol. 11, pp. 1146–1149, 2009. [Online]. Available: http://dx.doi.org/10.1016/j.elecom.2009.03.042

[4] M. Neruda, L. Vojtech, “Verification of surface conductance model of textile materials”, *Journal of Applied Research and Technology*, vol. 10, pp. 579–585, 2012.

[5] L. Vojtech, M. Neruda, “Application of shielding textiles for increasing safety airborne systems - limitation of GSM interference”, *in Proc. 9th Int. Conf. Networks*, Los Alamitos, 2010, pp. 157–161.

[6] A. Laforgue, “All-textile flexible supercapacitors using electrospun poly (3,4-ethylenedioxythiophene) nanofibers”, *Journal of Power Sources*, vol. 196, pp. 559–564, 2011. [Online]. Available: http://dx.doi.org/10.1016/j.jpowsour.2010.07.007

[7] *Battery separators*, Elmarco nano for life, 2013. [Online]. Available: http://www.elmarco.com/application-areas/battery-separators

[8] *Chemical Resistance Chart PVDF*, Zeus, 2013. [Online]. Available: http://www.zeusinc.com/technicalservices/technicalbulletins/chemicalresistanceofpolymers/chemicalresistancechartpvdf.aspx

[9] K. Yuri, Y. Mototani, J. Asaoka, “Alkaline battery having a gelled negative electrode”, U.S. Patent 5 587 254, 1996.

[10] V. Krejcik, *Technologie pro II. a III. rocnik ucebni obor galvanizer*. Prace, Praha, 1963.

[11] D. K. Hamilton, T. Wilson, “Three-dimensional surface measurement using the confocal scanning microscope”, *Applied Physics*, vol. 27, no. 4, pp. 211–213, 1982. [Online]. Available: http://dx.doi.org/10.1007/BF00697444

[12] B. P. Artamonov, M. S. Grilikhes, F. S. Kontorovich, B. K. Filanovskii, “Electrodes with burned-in platinum for contact conductometry”, *Biomedical Engineering*, vol. 5, no. 6, pp. 377–378, 1971. [Online]. Available: http://dx.doi.org/10.1007/BF00560006