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Cathode material for lithium ion accumulators prepared by screen printing for Smart Textile applications

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HIGHLIGHTS

- Thin, flexible and lowcost cathode for accumulator designed for Smart Textile application.
- The novel screen printing ink for mass production of cathode electrode was developed.
- $LiFePO_4$/PEDOT:PSS cathode enable fast charging and high performance accumulators.

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ABSTRACT

The presented study is focused on the development of $LiFePO_4$ based cathode for thin and flexible screen printed secondary lithium based accumulators. An ink formulation was developed for the screen printing technique, which enabled mass production of accumulator's cathode for Smart Label and Smart Textile applications. The screen printed cathode was compared with an electrode prepared by the bar coating technique using an ink formulation based on the standard approach of ink composition. Obtained $LiFePO_4$ cathode layers were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and galvanostatic charge/discharge measurements at different loads. The discharge capacity, capacity retention and stability at a high C rate of the $LiFePO_4$ cathode were improved when Super P and PVDF were replaced by conductive polymers PEDOT:PSS. The achieved capacity during cycling at various C rates was approximately the same at the beginning and at the end, and it was about 151 mAh/g for cycling under 1C. The obtained results of this novelty electrode layer exceed the parameters of several electrode layers based on $LiFePO_4$ published in literature in terms of capacity, cycling stability and overcomes them in terms of simplicity/industrial process ability of cathode layer fabrication and electrode material preparation.

1. Introduction

In recent two decades, the printed/coated functionalities have slowly penetrated the market through simple printed electronic systems targeted for daily consumption products (Smart Labels, Smart Textile), human health care or advertising. These types of functional products/applications are usually based on combinations of various structures like solar cells, electroluminescent light sources, transistors, radio-frequency identification (RFID), sensors, passive components, etc. Although it is actually possible to print a large number of these functional structures, in order to achieve the desired functionality of the developed systems (Smart Labels, Smart Textile, etc.), the printed functionalities are frequently combined with devices (MicroController Unit (MCU), diodes, etc.) common in surface mount technology (SMT). The majority of these functional "Smart Systems" usually need a source of electrical energy which exhibits good properties (mainly) in terms of flexibility, discharge capacity and stability at relative low price.

These thin, flexible, low-cost energy sources generally follow the traditional technology of batteries and accumulators, including

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used active materials. The major differences between the conventional form of electrical energy sources and printed electrical energy sources are given by application forms of collectors, electrode materials, separators, and electrolytes. In literature and at the market, there are numerous examples of printed batteries/accumulators from companies like Blue Spark, Enfucell, Power Paper, PowerID, Prelonic, Solicore, ITSUBO/Hatanaka Electric. The actual electrochemistry and characteristics of the batteries/accumulators are commonly influenced by the target application, working voltage, demands for capacity and availability of proper printing materials.

The preparation of various types of primary printed batteries is described in literature. The majority of them are based on the zinc/manganese oxide system called “alkaline” battery, which could be considered as a primary cell. There are several approaches to the preparation of given cells, especially to the preparation of selected layers, where gel based type electrolytes [1], or ionic liquids (IL) based electrolytes are used [2,3], or are prepared on various substrates as paper [4] or polyethylene terephthalate (PET) substrates [5]. The other common types of primary printed batteries are based on systems Zn/Ag_2O [6], Zinc-Air [7] or Li primary battery prepared by Ref. [8] using Li metal anode and MnO_2 as a cathode material.

A rechargeable Zn/MnO_2 accumulator was printed by Wang [9] using the flexography technique where an IL was used as an electrolyte. The other type of flexible accumulator based on a Nickel Metal-hydride cell was developed by Wendler [5] in cooperation with Varta.

Most of thin flexible accumulators are usually based on lithium electrode materials which follow chemical substances used in classic conventional accumulator applications. Lithium-ion accumulators have been commercially used since the early 1990s. The spectrum of usage of lithium-ion accumulators increases with the increasing demands on the amount of supplied energy, and also due to the gradual improvement of their properties lithium accumulators replace other types of accumulators (Ni–Cd, Ni-MH) from the market [10]. The most common application for this type of accumulators is nowadays especially in portable devices such as electric shavers, cell phones, tablets and laptops. Their expansion into flexible electronic devices and smart clothing is expected in the future. The first commercially available and still most widely used cathode material for lithium-ion accumulators is the cathode material $LiCoO_2$ (LCO) [11]. This material with a layered structure has a high theoretical capacity of 272 mAh/g and a stable discharge plateau at 3.88 V vs. Li. However, the full capacity cannot be fully used because of the layered structure; it would cause irreversible damage to the material structure and therefore the practically achievable capacity is about 140 mAh/g. Another disadvantage of this material is the high cost due to the presence of Co, instability when it is exposed to high temperature and instability during overcharging [12]. The $LiFePO_4$ (LFP) material was discovered in 1997 during the search for an alternative material without these weaknesses. This material is characterized by greater stability during thermal stress thanks to the olivine structure as well as lower costs, and it is more environmentally friendly. Another advantage of this material is its high theoretical capacity of 170 mAh/g. The disadvantage is the discharge plateau which is lower than the one of $LiCoO_2$; it means around 3.3 V vs. Li [13]. Thanks to its structural stability and therefore higher user safety, this material is a very suitable candidate for the use in wearable smart clothing. The literature describes different types of Li based batteries. Hu prepared accumulators based on $Li_4Ti_5O_{12}$ and $LiCoO_2$ as electrode materials where paper was used as a separator and carbon nanotube (CNT) free-standing film as a current collector [14]. The spraying method of preparation of an accumulator using $Li_4Ti_5O_{12}$ and $LiCoO_2$ was demonstrated by Singh et al. [15] The screen printing technique for fabrication of $Li–O_2$ accumulators using Li_2O_2 ink formulation was used by Jung et al. [16] Maximal discharge capacity 147 mAh/g was obtained for screen printed cathodes based on $LiCoO_2$ modified by carbon coating prepared from pyrolysis of resorcinol in studies published by Park [17–19] Pouch-type flexible screen printed accumulator using $LiCoO_2$ was fabricated by Kang [20]. This print technique was used by Lee [21] for printing a $Zr/LiCoO_2$ cell, where the charging/discharging characteristics were enhanced by addition of 5% of silver flakes. The $LiCoO_2$ electrode printed by the inkjet printing technique was prepared by Huang [22] with initial discharge capacity 120 mAh/g. Gu et al. [23] fabricated a cell from $LiFePO_4$ using inkjet printing technique. They obtained higher efficiency with a collector based on CNT/paper (−130 mAh/g at 1C) than with a classic Al collector (−95 mAh/g at 1C). The same technique and electrode based on carbon-coated $LiFePO_4$ for the cathode was used for the preparation of a porous electrode, where the discharge capacity of 150 mAh/g at 1C was obtained with $LiPF_6$ electrolyte [24].

In our R&D activities, we are focused on Smart Label and Smart Textile applications. Majority of proper MCUs, which represent “the heart” of an electronic system in Smart Label or Smart Textile applications require operation voltage in the range from 2 to 4 V. These demands of the given electronic systems could be satisfied by a serial connection of above mentioned Ni-MH or Zn/MnO_2 rechargeable accumulators, or especially, by using only a single Li accumulator based on the above described materials. Taking into account the demands on thin, flexible, low price energy sources and workflow fluency of the production process, the strong advantage is to produce these Li accumulators using the same production technology and production machinery which is used for printing of other parts/functionalities of Smart Systems within the printing house facilities. Respecting this, low-cost production of Smart Labels or Smart Textile products combined with Li accumulators printed by screen printing technique could be a proper solution.

The presented study is focused on the preparation of printed flexible electrode based on $LiFePO_4$ as a material with relatively good acceptance of ambient conditions during the fabrication process. The conductivity of $LiFePO_4$ is generally relatively low and it is even decreased by the presence of binder in the electrode layer. Binders for $LiFePO_4$ are usually non-conductive polymers as carboxymethyl cellulose (CMC) [24–28], poly(vinylidene fluoride) (PVDF) [19,29,30], poly(vinyl alcohol) (PVA) [19], poly(ethyleneimine) (PEI) [31], poly(methyl methacrylate) (PMMA) [30], poly-acrylic-co-maleic acid (PAMA) [24,27], poly(acrylic acid) (PAA) [19,28,29,32], or SBR as an adhesion promoter [32,33]. For this reason, the conductive interconnection between the particles and collector is enhanced by the addition of a carbon based material (−10% wt/wt) [24,27,29,30] or by coating of $LiFePO_4$ by carbon [17,18]. On the other side carbon and especially polymer binder present non active parts of cathode and decrease the specific values of capacitance in comparison to the theoretical limits.

These problems are solved by the novelty approach of our study, where the poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is used primarily as a binder and conductive part at the same time. The developed electrode material exhibits high capacity and it is capable to provide high current with a relatively small drop of capacitance. The ink formulation was developed for the screen printing technique for easy transfer to industrial scale.

The screen printing technique was used because it is the most used technique in printed electronic area and it is widespread in printing houses too. A next advantage is its versatility in terms of the printed layer thickness and the possibility to create various patterns/structures. The principle of screen printing technique is given by pushing of ink through open apertures/areas of the stencil to the printing substrate. The amount of transferred ink is mainly