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Self-writing smart labels employing ambient water harvesting

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ABSTRACT

Lateral anodic oxidation is a recent display technique with potential utility in the development of self-writing smart labels. This process requires water for activation, and the labels are typically operated at elevated humidity. To increase the operating humidity range of labels based on this mechanism, we incorporated a thin water harvesting layer to extract the necessary water from the ambient atmosphere. We examined the effect of relative humidity on the display process for several types of water harvesting layers. Labels based on lateral anodic oxidation of aluminum could be successfully operated under relative humidity down to 11% and the overall dependence of the devices on the relative humidity was reduced.

1. Introduction

Smart labels based on radio-frequency identification technology (RFID) are widely used for wireless identification of products and packages [1,2]. This technology was first described by Stockman [3] and has been continuously improved to the current state of the art [4]. The optimization of the manufacturing process of RFID-tags with the ambition of low cost production is a fundamental field. An encouraging approach for very low-cost devices is the inkjet-technology for printing the electrical elements on a polymer substrate [5,6].

Self-writing smart labels based on doping front migration were first reported by Knoll [7] and extended by Knoll colleagues [8,9]. The process occurs in an encapsulated sandwich consisting of an activation layer that exhibits a visually detectable sharp color change during the migration process and a migration layer for transportation of the doping agent. In later designs the polymer-based activation layer has been replaced by a nanoscale aluminum layer that undergoes electrochemical oxidization in one dimension in a process known as lateral anodic oxidation [10]. During the oxidation, the aluminum changes from an opaque metallic film to a transparent oxide. The potential required for the process is provided by an electrochemical cell composed of a graphite cathode and the self-consuming aluminum electrode [11].

In this paper we describe self-writing smart labels equipped with thin water harvesting layers containing a hygroscopic inorganic salt immobilized in a polymer film to collect water from the ambient atmosphere, providing self-contained operation of the labels. Water harvesting by a hygroscopic agent in dehumidification devices is a well-known process [12–15]. Zhang et al. [16] reviewed the use of cross-linked polyvinyl alcohol membranes containing hygroscopic agents for dehumidification. The concept was extended in this work by the development of a thin electrolyte layer that acts as both an electrolyte for the oxidation process and as a water harvesting layer. This is the final important step in preparing a totally independent self-writing smart label that may be directly applied to products and packages.

2. Theory

A smart label based on lateral anodic oxidation of aluminum is depicted in Fig. 1. The activation layer consists of a partially encapsulated nanoscale aluminum layer. In the presence of a counter electrode with a higher standard potential than aluminum, the aluminum is oxidized.

The potential of the counter electrode is provided by the electrochemical reduction of oxygen at graphite [17]:

$$O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^- \quad (-0.065\,V)$$

For the pitting corrosion of aluminum a potential between -0.65 V and -0.69 V is reported [18] so that a cell voltage of 0.6 V is obtained [11].

The encapsulation forces the oxidation process to proceed in one dimension. The advancing interface between the transparent aluminum oxide and the unoxidized metal film is very sharp.

The material used for the water harvesting layer is composed of a hygroscopic agent to harvest water vapor from the ambient atmosphere and a binder to immobilize the hygroscopic agent.

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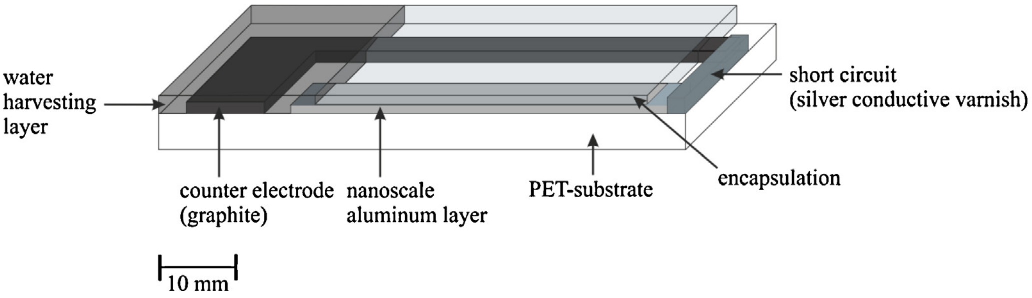

Fig. 1. Self-writing smart label with applied water harvesting layer.

A variety of alkali halides were employed as the hygroscopic agent. The minimum relative humidity required for operation is dependent on the hygroscopicity of the alkali halide and is correlated to the relative humidity of a gas phase in equilibrium with the saturated salt solution [19,20]. Selecting from a variety of halide salts makes it possible to tune the operating conditions for a specific application.

3. Materials and methods

The devices were constructed from a commercially prepared film consisting of an aluminum layer (approx. 20 nm) on a polyester substrate (GBC Color Pouch, ACCO Europe). The aluminum electrode pattern was formed into the film using a laser (Nd:YAG, $\lambda = 1064$ nm). The counter electrode was formed from a mixture of acrylic resin (Wilckens) and graphite powder GSI 70 (weight ratio 3:7) and was applied using a stencil. The devices were encapsulated by hot lamination.

3.1. Water harvesting layers

Hydroxyethyl cellulose solution ($M_V = 90.000$, D.S. 1.50, Brookfield viscosity: 75,000–150,000 cps (5 wt%, 25 °C)) was obtained from Sigma–Aldrich. Wheat starch was purchased from FAGRON GmbH&Co.KG and polyacrylic acid (Carbomer 50,000, Carbopol 980) was obtained from Caelo. Lithium bromide, lithium chloride, and sodium bromide were purchased from Sigma–Aldrich.

The water harvesting layer solution using hydroxyethyl cellulose as a binding agent was prepared by combining hydroxyethyl cellulose and 0.5 M lithium bromide solution (weight ratio 1:9) and stirring at 50 °C for 1 h.

The wheat starch-based water harvesting layer solution was prepared by stirring a mixture of wheat starch and either 2.0 M lithium chloride solution or 4.0 M sodium bromide solution (weight ratio 1:24) at 95 °C for 30 min. After cooling, 1 wt% of BYK-378 (BYK) was added to the solution to reduce its surface tension to facilitate the film application.

Water harvesting layer solutions based on polyacrylic acid were prepared by mixing polyacrylic acid and 1.25 M lithium bromide solution (weight ratio 1:19) and stirring for 60 min at room temperature.

To offer a defined coated area the substrate is masked by an adhesive film (thickness: 50 μm) before the water harvesting layer solution is applied by a Mayer bar (100 μm). The resulting wet thickness is 150 μm (thickness of the adhesive film for masking + application thickness of the Mayer bar). The layer is dried for 24 h at a relative humidity of <5% and the resulting dry thickness is measured with a profilometer (Dektak XT, Bruker).

For humidity control saturated salt solutions were used to provide a defined equilibrium relative humidity in a chamber (lithium chloride: 11% [21]; calcium chloride: 31% [22]; sodium thiocyanate: 47% [23]; sodium bromide: 58% [21]; sodium chloride: 75% [21]; potassium chloride: 84% [21]).

The measurement of the migrations lengths is performed by a scanning interface with optical analysis by computer-software.

4. Results and discussion

The dried mechanical stable water harvesting layers exhibits a thickness of 15 μm (hydroxyethyl cellulose-based), 6 μm (wheat starch-based) and 4 μm (polyacrylic acid-based water harvesting layer).

In Fig. 2 the status of a self-writing smart label at different times of operation is shown. The oxidation front appears very sharp and flat.

Figs. 3–6 depict the behavior of the migration lengths of the moving interface between the transparent aluminum oxide and the unoxidized aluminum film depended to the time [$l(t)$] and the migration lengths to the ambient relative humidity [$l(\varphi)$] of devices supplied by various types of water harvesting layer.

Our objective was to achieve minimal dependence of the oxidation velocity on relative humidity. Water harvesting layers based on hydroxyethyl cellulose and lithium bromide (Fig. 3) displayed a distinct dependence on $l(\varphi)$. When φ was equal to 31% lateral oxidation begun after a delay of approximately 10 h due to the high

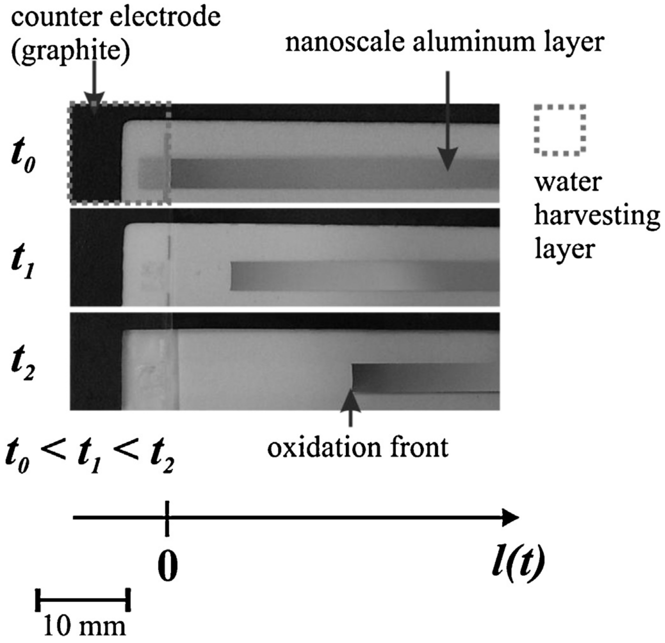

Fig. 2. Photographs of self-writing smart label with applied water harvesting layer at different times t_x during lateral anodic oxidation.