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Self-powered electrochromic display as an example for integrated modules in printed electronics applications.

Martin Möller^a, Nigel Leyland, Gavin Copeland, Micheál Cassidy

NTERA Limited, 58 Spruce Avenue, Blackrock, Dublin, Ireland

phone +353 1 2137 538

fax +353 1 2137 564

PACS

82.47.-a - Applied electrochemistry

82.47.Tp - Electrochemical displays

82.47.Cb - Lead-acid, nickel-metal hydride and other batteries

Short title

Self-powered display for printed electronics

Abstract

The growing market for flexible electronics devices is asking for reduction of manufacturing process complexity. One way to reduce complexity is to decrease the number of single components of a device by using integrated modules, i.e. device components providing multiple functions. In this article, the concept of a self-powered electrochromic graphics display device is demonstrated. The device is based on a three electrode system comprising an electrochromic electrode, a battery anode and a battery cathode, all in contact with a common electrolyte. The electrochromic electrode can be charged and discharged directly when connected to either the anode or cathode. Such a self-powered display integrates the functions of both a display and a battery. As part of a flexible electronics device, a self-powered display would be able to power other components, such as driver electronics.

Introduction

Development of modern flexible electronics devices like smart cards or smart labels, require the integration of a display, a power source and electronics onto flexible substrates.

Substantial industrial effort is being expended towards the most cost effective way to solve this problem by providing, for instance, an all printable device, whereby all components are built up step by step onto the same substrate. NTERA's NanoChromicsTM display technology

^a e-mail: martin.moeller@ntera.com

already meets the requirements of an all-printable and flexible display device architecture for static graphics and segmented alpha-numeric applications.

In recent years, a lot of progress has been made towards printable electronics components [1-9] like transistors, circuits and RFID and other devices such as displays¹[10, 11], batteries [12, 13] and solar cells [13-15]. Out of all the research fields involved, the most challenging is the development of complex circuits with computing power suitable for sophisticated applications. Thus, some of the early flexible electronics applications will still need traditional silicon based electronics on flexible support.

However, development of single components on their own will not lead to commercial products. This is why functional integration of components deriving from the interdisciplinary fields is another important key. With regard to fully printable electronic applications, functional integration can be seen from a broad perspective. In traditional silicon based electronics, integration is more or less limited to the combination of electronic circuits onto a single chip due to the way it is manufactured. The final electronic device needs then to be assembled from multiple components, including the chip. Manufacturing solely based on printing processes does not require assembling of components and thus, is one important route to arrive at cost effective solutions for flexible electronic devices. Furthermore, in contrast to assembling, printing allows for comprehensive integration of different device components. More precisely, printing eliminates the need to restrict focus to the electronic circuits domain and allows the creation not only of “integrated circuits” but of “integrated modules” to realise flexible electronic devices with minimum complexity.

One example of such an integrated module is presented in this article in the form of a combination of an electrochromic display and a battery.

Experimental

For commercial reasons, the experimental part is not described in full detail.

Printing: A masking layer, an electrochromic electrode layer, an anode layer, a cathode layer and silver layers for electrical contacts were printed onto a polyester (PET) film using a screen printing method. The films were dried at 130 °C for several minutes. The opaque masking layer was of a similar colour to the electrochromic electrode and formed the inverse image of the display. The electrochromic ink used contained sub-micron sized TiO₂ particles to provide optical diffuse reflection and electrochromic pigments. The electrochromic pigment used was a viologen derivative attached to metal oxide nanoparticles via a

¹ www.ntera.com

phosphonic acid group. Zn particles were used as anode material and MnO₂ particles were used as cathode material. Both, anode and cathode inks, contained graphite and carbon black particles to provide a conducting network.

Device assembling: The areas of the electrodes were covered with a cellulose cloth. Some drops of an aqueous electrolyte containing ZnCl₂ and NH₄Cl and glass beads, used as spacer, were placed onto the cloth. Subsequently, the device was sealed under vacuum using a second PET substrate and UV-curable glue.

Electrochemical measurements on single electrodes of ~1 cm² geometric area were carried out using a Solartron 1285 bipotentiostat, a Ag/AgCl in 3 M KCl reference electrode, a glassy carbon counter electrode and the same electrolyte as used in the device described above. The electrolyte was purged with N₂ prior to the measurements.

Results and Discussion

In the past, an electro-optical display was powered via electrical connections to an external power source. In contrast to other display techniques, an electrochromic display is an electrochemical device. This fundamental aspect is shared between electrochromic displays and batteries. As a result, an electrochromic electrode and battery electrodes can be part of the same electrochemical system with a common electrolyte. In such a self-powered display [16], the electrochemical energy range of the electrochromic electrode from bleached state to coloured states needs to be located in between the electrochemical energies of the anode and cathode (Fig. 1). Unlike a battery electrode, the electrochromic electrode is optimised to exhibit a low electrochemical capacitance combined with a significant colour change. In transparent electrochromic systems, the colouration efficiency is defined as

$$\eta = \frac{\Delta A(\lambda)}{Q} \quad (1)$$

where Q is the displaced charge and $\Delta A(\lambda)$ is the absorbance change at a given wavelength [17]. Qualitatively, a similar relationship applies for reflective devices, though light reflection follows more complex rules compared to light absorbance. An electrochromic electrode based on viologen adsorbed onto a conducting support with low electrochemical capacitance typically shows colour changes suitable for display applications at charge densities of 1-2 mC/cm². This observation can be related to the typically high specific absorbance coefficients for viologens around $\epsilon(\lambda_{\max}) \cong 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ [17, 18]. Depending on the purpose of a specific device application, the composition and size of the battery electrodes need to be dimensioned accordingly to support a sufficient number of operation cycles.

With viologen as the electrochromic material, colouration of the display is achieved by electrical connection of the anode and the electrochromic electrode (Fig 1a). In this situation, the electrochromic electrode acts as a cathode, but comprising a very low capacitance as described above. Upon connection of electrochromic electrode and cathode, the former acts as an anode and bleaches to its original state (Fig. 1b).

Since in such a self-powered display the functionality of a battery is included, it could also be used as the generic power source for all components of a device application (Fig. 2). Such components could be the electronic device driver, a sensor and others. Additionally, power collecting components such as solar cells or RFID antenna/rectifier circuits acting as a wireless power receiver could be used to recharge the self-powered display – rechargeable battery electrodes assumed.

A display device representing the basic concept of self-powered electrochromic displays is shown in Fig. 3. The initial voltage between anode and cathode was 1.5 V. When connecting anode and cathode directly for a few seconds, an average short circuit current of ~1 mA was observed. Switching times of ~5 s were found for colouring and bleaching of the electrochromic electrode by direct connections to anode and cathode, respectively. Once switched to the “on” state, the colouration persists at open circuit.

In this example, the three electrodes (electrochromic electrode, anode and cathode) are arranged side-by-side on the same substrate. The advantages are a good electrical separation of the different electrodes and a minimum number of printing steps. However, the configuration shows limitations regarding switching times in the range of a few seconds due to geometric boundary conditions, i.e. a thin layer of electrolyte compared to long distances for the charge transport. A stacked configuration with intermediate separation layers would involve more printing steps and the separation layers to be virtually ideal electrical insulators. In return, due to the different geometry, faster switching would be possible and space requirements would be reduced.

Results of electrochemical measurements on single electrodes of the self-powered display are shown in Fig. 4. The half wave potential for the electrochromic electrode was estimated at -0.44 V from the cyclic voltammetry data and the equilibrium open circuit potentials of the anode and cathode were found at -0.96 V and +0.63 V, respectively. Thus, the driving voltage for bleaching is about twice as large as for colouring the device. Such a significant difference could not be found for the colouring and bleaching times in the completed device (Fig. 3). This suggests that the surplus of driving voltage for bleaching is

compensated by other effects like resistances within the electrodes and/or the kinetics of the different electrochemical reactions.

Conclusion

The self-powered display described in this article shows one of the early steps towards integrated modules for cost effective manufacturing of flexible electronic devices. A display-battery combination is able to reduce space requirements as well as the number of manufacturing steps and also significantly reduces the integration complexity of the display and power source for a wide range of flexible electronic devices. Current efforts in this field are focused on the development of fully printable solutions.

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Figure Captions

Fig. 1: Generic concept of a self-powered electrochromic display. The area surrounded by the hatched frame indicates the electrochemical system with a common electrolyte. A switch allows to (a) reduce and (b) oxidise the electrochromic electrode.

Fig. 2: Generic concept of a self-powered electrochromic display incorporated into an electronics application. The area surrounded by the hatched frame indicates the electrochemical system with a common electrolyte. (a) Electronic device driver to control the display and other components. (b) Placeholder for other components like, e.g. a solar cell or a sensor.

Fig. 3: Example of a self-powered electrochromic display in (a) “off” and (b) “on” state. Top electrode (black): Zn/C, center electrode (white): electrochromic electrode, bottom electrode (black): MnO₂/C.

Fig. 4: Electrochemical characterisation of single electrodes. Cyclic voltammetry (10 mV/s) of the electrochromic electrode (solid line) and positions of the equilibrium open circuit potentials of the Zn/C electrode (dashed line) and the MnO₂/C electrode (dotted line).

Fig. 1

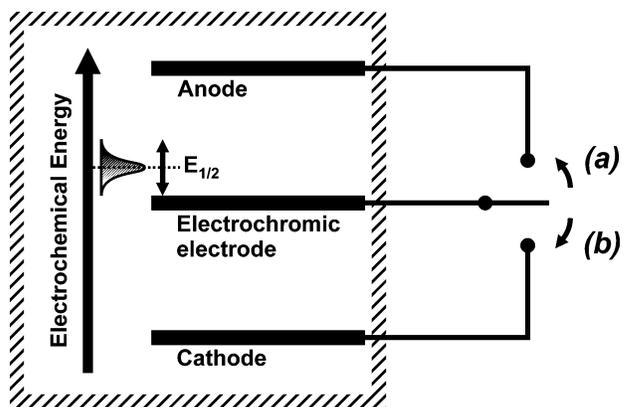


Fig. 2

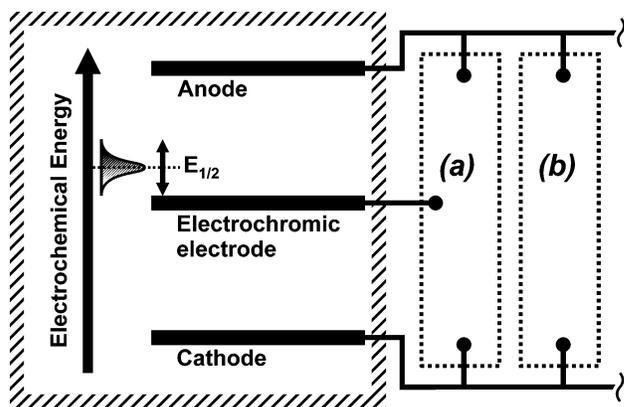


Fig. 3

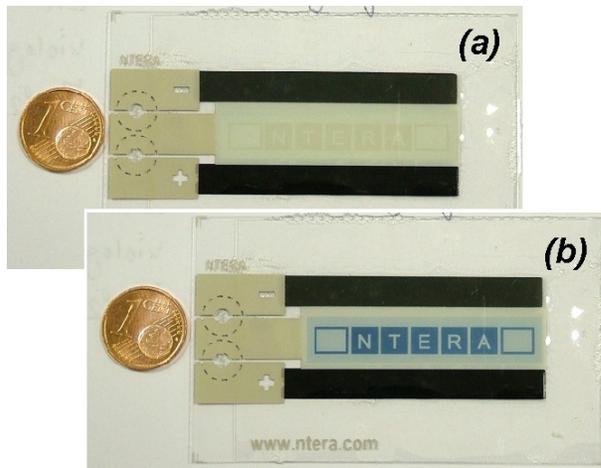


Fig. 4

