

WATER-BASED ELECTRONIC PAPER AS LOW-COST MULTI-COLOR SCREENS

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Abstract Electronic paper devices also known as electrochromic devices are known for their ability to change color with option to remain in certain color state even after the electrical power has been lifted. Traditional devices such as electrochromic windows used mechanisms like electrophoresis or intercalation and use special materials such as water-less electrolyte, and transparent conductive materials (TCM). As such, these devices can sometimes be relatively difficult to assemble, especially in developing countries, where such materials are harder to come by. Recently, certain improvements have been made by using alternative electrode positioning, that they do not require TCM. Presented here is a novel type of electronic paper that is recyclable, can be constructed as a monochrome or multi-color device and can be scaled accordingly to desired screen size. Presented electronic paper, is a semi-open electrochemical device, which uses pH indicator dyes and water-salt solution, combined with easily obtained sheet steel.

Keywords:

pH indicator,
electronic paper,
stainless steel,
alternative
electrode
positioning,
water electrolyte

1 Introduction

Electrochromism is the phenomena, where a device can change coloration under applied electric current or potential, with additional ability to sustain newly adopted color even after the power source has been disconnected. As such, electrochromic devices (ECDs) that exhibit such qualities are known as electrochromic devices and are in principle much different compared to more traditional fast responding liquid crystal displays (LCDs) or light emitting diodes (LEDs). (Kim and Song) (Krasnov) Due to their unique behavior, they can be used in much more different applications compared to more conventional screen technologies such as smart windows and electronic paper. First electrochromic devices showed up at start of 1960s, (Kumamoto et al.) (Platt) where they had relatively limited use due high potentials requirements and slow response time. Vast improvement was shown with introduction of novel materials such as tungsten trioxide (WO_3) and new sol-gel synthesis developed first by Hersh and coworkers (Hersh et al.) which promised development of novel devices and its widespread use. Shortly after, all-polymer devices were developed, which utilized polymer based transparent conductive electrodes (TCE) using poly(3,4-ethylenedioxythiophene) (PEDOT) and other polymers. (Pei et al.) (Kobayashi et al.) Due to certain materials cost, namely TCE materials, adoption of these devices was quite slow, and once the battery technology developed enough to support high potential demand of LCDs, making ECDs less interesting. Recently, several attempts have been made to avoid use of TCE, which could substantially reduce production cost of different devices, from solar cells, as well as ECDs. (Rozman et al. "Novel Geometric Approach for Photosensor Construction Based on Dye-Sensitization of TiO_2 Nanoparticles on Stainless Steel") (Rozman et al. "Flexible Electrochromic Tape Using Steel Foil with WO_3 Thin Film") In a paper of Lukšič et al it was shown that it is possible to construct a device, that does not require TCE. (Rozman et al. "An Inverted Sandwich Electrochromic Device Architecture Does Not Require Optically Transparent Electrodes") In addition, presented device utilized salt-based water electrolyte, combined with pH dye that uses electrolysis as a color changing mechanism, thus avoiding the use organic solvents. By combining different pH dyes it could be possible to find a combination of coloration responses, where all the dyes share the same basic color that can be interpreted as bleached state, while the tinted state of each individual assembled cell is proportional to used pH dye. Due to already established lists of known responses for individual pH, it is easy to find a dye with appropriate

coloration response, (Khan et al.) (Van der Schueren and De Clerck) but finding the right combination of dyes to assemble such device might still be difficult. This is due to the reason, that selected pH dyes should not interact with electrolyte electrodes or each other since this could severely affect the longevity of the device. Here, we present a method on how to assemble a multi-color electrochromic device, which incorporates several electrochemical semi-cells with added dye, where semi-cells share the same electrolyte. In addition, assembled device utilizes so-called “inverted geometry”, with which it is possible to avoid using TCE.

2 Materials and methods

2.1 Materials

Technical materials such as stainless steel foil type AISI 316 (TBJ Industrieteile GmbH, Germany) tissue paper (Paloma multi fun, Slovenia), insulation tape (Tesa, Germany) and microscope slide glass (IsoLab GmbH, HE-2400, Germany) have been obtained from different suppliers. Chemicals such as sodium acetate (99.9%) and ammonium sulphate (99.9%), ethanol (99.8%) along with pH dyes methyl red (99.9%), bromothymol blue (99.9%), α -naphthophtalein (99.9%) were obtained from Sigma-Aldrich.

2.2 Device assembly

Before device assembly different pH dye solutions as well as electrolytes were prepared. Two different electrolytes were prepared using sodium acetate and ammonium nitrate, both dissolved in separate measuring flask with concentration of 2.5 M. For completed 4-pixel device 2.5 M sodium acetate was used, while for individual pixel device assembled under instructions from literature (Rozman et al. "An Inverted Sandwich Electrochromic Device Architecture Does Not Require Optically Transparent Electrodes") that used methyl red dye, 2.5 M ammonium sulphate was used. Next, pH dyes were prepared by dissolving of 0.1 g of selected dye in 20 mL of ethanol each in separate beaker and stirred until the dye was dissolved. The same mass was used for all selected dyes: Bromothymol blue (BM), Methyl red (MR) and α -Naphthophtalein (AN). Each solution was then placed in its own measuring flask. For each individual dye, a paper patch measuring 5 mm by 25 mm was cut using scissors. Each patch was then soaked with the individual pH dye

and let 20 minutes to dry on air. One additional patch has been made that was first soaked in bromothymol blue and was then additionally sprinkled with dropper using α -Naphthoptalein. This 4th patch was done to be used so the device could demonstrate 4-pixel operation and was not characterized in details. After dyed paper preparation, four electrodes were cut using scissors, measuring 5 mm by 25 mm each, and they were adhered on one side with insulation tape. Each electrode was wrapped on the end of the electrode with dyed paper in such way, that an area of 5 mm by 5 mm was covered. Next, a counter electrode that measured 25 mm by 10 mm was cut. Following counter electrode preparation, working electrodes with wrapped paper were positioned on counter electrode and were then soaked with 2.5 M sodium acetate using dropper. The entire device was encapsulated into two pieces of glass measuring 35 mm x 35 mm, with excess liquid removed using paper towels. Constructed 4-pixel device measured 10 mm x 10 mm and used „inverted geometry“ assembly approach.

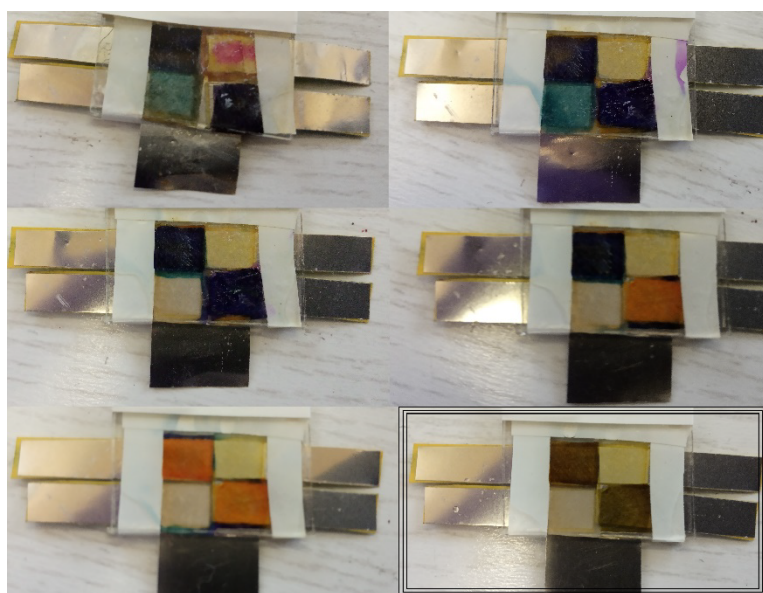


Fig. 1: Assembled water-based ECD in various coloration states. The initial color state after completed assembly is presented in lower right corner.

Surce: own.

2.3 Characterization methods

Device testing was done using variable power supply PS-302A (Voltcraft GmbH, Germany), while electrochemical measurements were done using Autolab PGSTAT128N (Metrohm, Switzerland) on 5 mm x 5mm devices, that represented individual pixels. Spectrophotometric measurements were done using Cary 50 (Agilent, USA) with fiber probe attachment for specular reflectance measurement.

3 Results

3.1 Cyclic voltammetry

Voltametric measurements were first done to determine behavior of stainless steel electrodes in different electrolytes. 10 cycles were done in potential window between -4 and +4 V, with starting point at 0 V with reference connected directly on counter electrode terminal. It was determined that. In fig. 2 it can be observed that both electrolytes have inertial potential window between -2 and + 2 V, suggesting that the main reaction is electrolysis of water, where on positively charged anode the water splits into oxygen and hydronium ion ($3H_2O \rightarrow 2H_3O^+ + \frac{1}{2} O_2 + 2e^-$) where on negatively charged cathode, the water splits into hydroxyl ion and hydrogen ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$). The cathodic and anodic peaks for both Fig. 2a and 2b that are visible between +/-1.5 V and 2.5 V are belonging to gas reduction, either oxygen reduction or hydrogen oxidation, respectively. Only post-measurement inspection after 10 cycles showed that ammonium sulphate is more corrosive, which could be related to sulphate anions, which are more aggressive towards stainless steel compared to acetate anions. Despite having more artefacts, that were recorded during voltammetry in Fig 2a, that were due to gas build-up, the 2.5 M sodium acetate proved superior to 2.5 M ammonium sulphate. Additionally, 2.5 M ammonium sulphate had almost too high conductivity, resulting in increased current consumption while having no coloration response advantage. This can be observed as a signal cut-off below - 3 V and above + 3 V, in Fig. 3b, where potentiostat/galvanostat instrument was limited to maximum 40 mA/cm² to prevent excessive heating of tested device.

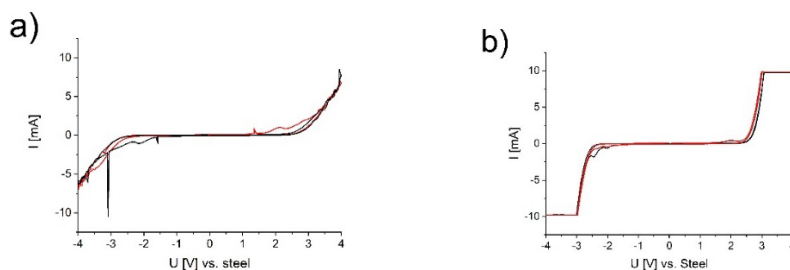


Fig. 2: Cyclic voltammetry of assembled 5 mm x 5mm device using 2.5 M sodium acetate (fig. 2a) and 2.5 M ammonium sulphate (fig. 2b) with AISI 316 stainless steel electrodes. Presented are 1st (black label) and 10th (red label) cycle.

Source: own.

3.2 Chronoamperometry

Chronoamperometry (Fig. 3) was performed with positive pulse of + 3.5 V and negative pulse of -3.5 V both lasting for 30 s and between each with 30 s waiting period. Potential polarity was altered after each pulse. This experiment was done to determine the conductivity and performance on two different devices, 2.5 M sodium acetate with bromothymol blue (black label) and 2.5 M ammonium sulphate with methyl red (red label) respectively. During 5 cycles of assembled device, it was observed that both devices have adequate coloration response, with no indications that any of the dyes would be affected due to electrolysis. After completing 5 cycles, it was determined that sodium acetate is less corrosive to stainless steel and was thus used as a preferred electrolyte.

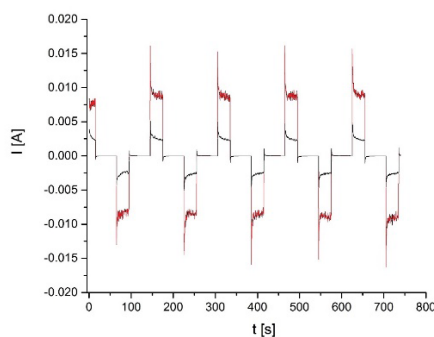


Fig. 3: Chronoamperometry of assembled 5 mm x 5mm devices. Presented are 2.5 M sodium acetate (black label) and 2.5 M ammonium sulphate (red label) 5 mm x 5 mm devices.

Source: own.

3.3 UV-Vis reflectance spectrophotometry

UV-Vis measurements of individual pixels of assembled 4-pixel device were done to determine change of coloration. The UV-Vis measurements were performed on an assembled 4-pixel device, with spectrums recorded for three pixels that had individual color, using Bromothymol blue, Methyl red, and α -Naphthophtalein. Since the constructed device used 2.5 M sodium acetate, the pixel dyed with methyl red performed less ideally, due to Methyl red low pH required for coloration change of around 4.6, while sodium acetate has relatively high measuring around 8-9. (Rozman et al. "An Inverted Sandwich Electrochromic Device Architecture Does Not Require Optically Transparent Electrodes") Nevertheless, device was successful in obtaining all required color changes, which can be seen in Fig. 4. Both Bromothymol blue and α -Naphthophtalein are yellow in acidic media, and colored in basic media, while Methyl red has reverse response with yellow coloration in basic media and red coloration in basic media. Main coloration difference can be observed at around 600 nm for Bromothymol blue, 650 nm for α -Naphthophtalein, while for Methyl red the main difference between both states can be visible in area between 400 to 500 nm.

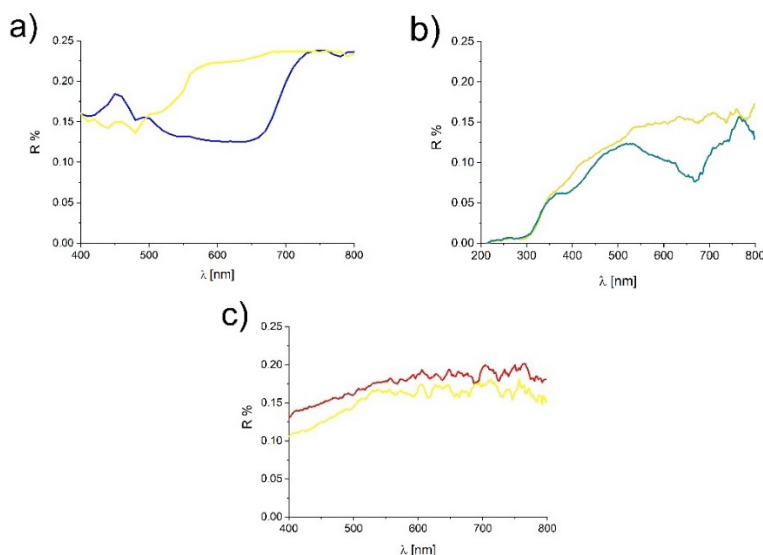


Fig. 5: UV-Vis spectrums of 4-pixel ECD device for various dyes: Bromothymol blue (fig. 4a), Methyl red (Fig. 4b), and α -Naphthophtalein (Fig 4c). For each label, appropriate visible color is used.

Surce: own.

4 Conclusions

It is possible to construct water based ECDs, that can have different coloration and could be potentially used as actual screens, and that despite marginal change in UV-Vis spectrum, coloration change of Methyl red was observable with naked eye. Results are suggesting that both Bromothymol blue and α -Naphthoptalein are most suitable for future use in development of water based multicolor screen, while Methyl red should be replaced with more suitable pH dye. In addition, such devices, could be made with relatively simple tooling and using traditional electrical engineering to connect several such devices into functional screens. Despite their relatively slow response, they could still be used in roles, where reaction time is less important, but large screen surface is desired. Such devices could be used for advertisement boards or other displays where low cost and simple development are a priority.

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