

# Integration of Supercapacitors to Trigger In-Situ Electropolymerization for Irreversible Visual Indicators

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**Abstract**— Printed supercapacitors (SCs) are demonstrated to activate 1x1 cm<sup>2</sup> Irreversible Visual Indicators (IVIs) based on four different monomer systems: 3,4-Ethylenedioxythiophene (EDOT), bis-3,4-Ethylenedioxythiophene (BiEDOT), 2,2'-Bithiophene (Bithiophene), and 2,2':5',2''-Terthiophene (Terthiophene). The key parameters which determine whether the IVIs can be fully activated ( $\Delta$  Optical Density > 0.9) are the activation potential, the coloration efficiency (CE) of the IVI's, and the initial voltage and charge density of the SCs. All four monomer systems can be fully activated by three of the printed SCs connected in series (3.55 V), but only BiEDOT and TerThiophene can be fully activated by two series connected printed SCs (2.35 V).

**Keywords**—Electrochromic Displays; Supercapacitors; Printed Electronics; Circuit Integration; Smart Labels; Irreversible Systems; Electropolymerization

## I. INTRODUCTION

Electrochromic indicators and displays have commercial interest in the logistics, retail, and healthcare sectors as a dynamic form to convey information [1]. While a traditional approach to produce electrochromic displays consists of depositing or coating the chromogenic material during the manufacturing process, researchers such as Sotzing have put forward the concept of 'in-situ' electropolymerization as a simpler route for electrochromic display fabrication [2]–[5]. Using this technique, an electrochromic polymer is formed inside of the display electrochemically after the device has been fully manufactured.

While in-situ electropolymerization has been demonstrated as a method to generate electrochromic displays for conventional reversible cycling [6], the color transformation produced in the electropolymerization process can be utilized to create an Irreversible Electrochromic Indicator (IVI). This is envisioned for use in applications such as spoilage labels, or tamper labels, where a stark color change is necessary that cannot be removed, see Fig. 1. Commercial application of IVIs requires integration with a switching circuit and a power source that can trigger the electropolymerization reaction during use. Over the past decade, researchers around the world have become increasingly interested in supercapacitors (SCs), since SCs are regarded as an alternative to batteries for electrical energy storage [7]. The benefits of SCs as a promising energy storage

system over conventional rechargeable batteries include high power density, light weight, exceptionally longer cycle life, lower internal resistance, short charge/discharge times, wide temperature range of operation, recyclability, and a low environmental impact [7]–[14]. While previous studies [15] have demonstrated reversible switching of electrochromic displays using SCs, electropolymerization requires a significantly greater voltage and charge than reversible redox switching of the corresponding homopolymer.

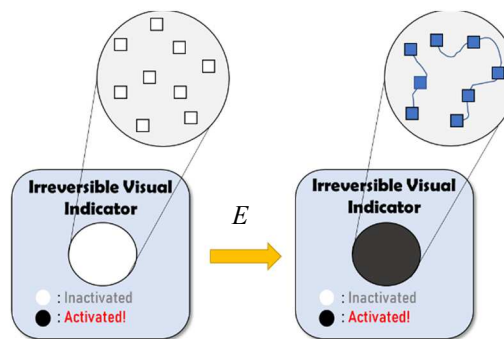


Fig. 1. Schematic of an irreversible visual indicator via electropolymerization

In this study, printed SCs are used to trigger in-situ electropolymerization of devices with four different monomer systems: 3,4-Ethylenedioxythiophene (EDOT), bis-3,4-Ethylenedioxythiophene (BiEDOT), 2,2'-Bithiophene (bithiophene), and 2,2':5',2''-Terthiophene (terthiophene). These monomer systems were selected as they present a broad range of activation potentials ( $E_a$ ) and coloration efficiencies (CEs). The results of the activation with the printed SCs are evaluated and compared to a 3 V coin-cell battery. Overall, the study finds that for high coloration efficiency monomer systems, SCs can deliver sufficient voltage and charge to fully activate 1 x 1 cm<sup>2</sup> indicators, making them a promising candidate for activation of in-situ electropolymerization indicators.

## II. MATERIALS AND METHODS

### A. Fabrication of Indicators

The electrolyte is composed of ethylene carbonate, propylene carbonate and lithium perchlorate in a 1:0.47:0.098

ratio. Gel electrolytes were formulated by incorporation of 9.95 wt% Zeospan 8030 triblock copolymer from ZEON Chemicals, and 0.5 wt% Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide photo initiator using a stainless-steel blade mixer. 10 mg/ml of monomer was mixed into the gel electrolyte.

Flexible devices were fabricated using a vertical device architecture composed of two 80  $\Omega$ -1 PET-ITO electrodes (Eastman, FLEXVUE) and a 220  $\mu$ m adhesive spacer material. The working area is a 1 cm<sup>2</sup>. The electrolyte is cured using a LOCTITE 500 W mercury vapor bulb for 120 s. Copper tape was added to improve the electrical contact to the power source.

### B. Fabrication of Supercapacitors

The authors have already published a detailed description of the process for fabricating and characterization of the printed SCs used in this study [16]–[19]. This paper provides only a brief overview of the fabrication process. A double-sided flexible Al/PET substrate was coated with graphite ink (Acheson Electrode PF-407C) as a current collector on the PET side, while the Al layer served only as a barrier. In order to form an electrode layer, activated carbon ink (Kuraray YP-80F) was applied on the current collector layer using an in-house formulation containing chitosan as a binder. The two layers were achieved using laboratory-scale doctor blade coaters. Afterwards, NaCl:H<sub>2</sub>O aqueous electrolyte and a paper separator were added, and the two electrodes were then heat-sealed upside down with an annealed adhesive material to form an SC of the electrochemical double-layer capacitor (EDLC) type.

### C. Measurements

Optical spectroscopy was performed on an Agilent Cary 300 UV-Vis Spectrophotometer. The activation of the indicators was measured by following the transmittance at 555 nm, the peak of human photopic vision. Potentiostatic and cyclic voltametric measurements were performed with an AUTOLAB PGSTAT100N potentiostat. The voltage of the SCs was measured using a FLUKE® 115 handheld multimeter digital CAT III 600 V display (counts): 6000.

## III. RESULTS AND DISCUSSION

### A. Electrical and Optical Characterization of IVI systems

Two key electrical properties for IVIs are  $E_a$  and CE. The  $E_a$  of an IVI is primarily determined by the oxidation potential of the monomer system, and the CE is primarily determined by the number of electrons transferred in each cross-linking step (typically in the range of 2.07–2.60 F·mol<sup>-1</sup> per monomer reacting [20]), as well as the length and absorptivity of the polymer formed. However, other parameters including the solvent, salt, monomer concentration, and electrical activation protocol can influence these values.

The first scan of cyclic voltammetry measurements of IVIs with all four monomers are shown in Fig. 2a. The onset of polymer film formation is identified by the rapid increase in the current density from monomer oxidation and subsequent cross-linking steps. The change in optical density as a function of charge during potentiostatic activation is shown in Fig. 2b. A

summary of the  $E_a$  and CE for all four monomers is shown in Table I. As the conjugation length of a monomer species increases, the oxidation potential decreases, fewer cross-linking steps are required to form the same length of polymer. Thus, the CE of BiEDOT compared to EDOT and TerThiophene compared to BiThiophene are more than double, and the  $E_a$  decrease by 0.5 and 0.3 V respectively.

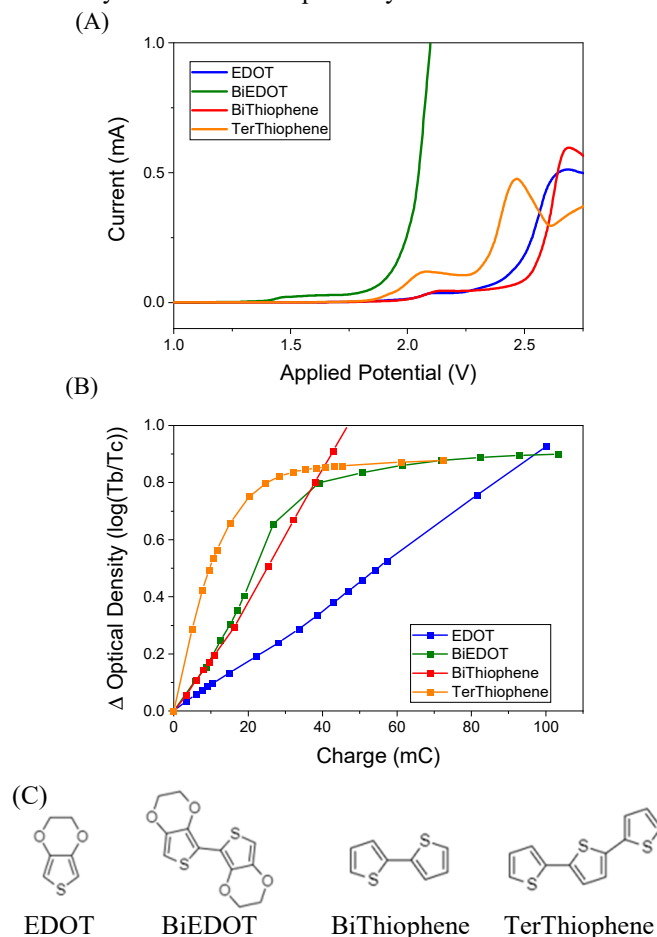


Fig. 2. (A) First forward scan of cyclic voltammetry of indicators at 10 mV/s (B) change in optical density at 555 nm as a function of current when activated potentiostatically at 3 V (C) chemical structure of EDOT, BiEDOT, BiThiophene and TerThiophene monomers.

TABLE I. KEY ELECTRICAL PROPERTIES OF IRREVERSIBLE INDICATORS BASED ON DIFFERENT MONOMER SYSTEMS

Monomer System	Activation Potential (V)	Coloration Efficiency (Cm <sup>2</sup> /C)
EDOT	2.5	9
BiEDOT	2.0	24
BiThiophene	2.6	21
TerThiophene	2.3	49

<sup>a</sup>. Measured at 555 nm during 3V potentiostatic activation

### B. Activation of IVIs with SCs and Coin-Cell Battery

The key electrical properties of SCs are the initial voltage ( $E_0$ ), capacitance (C), and equivalent series resistance (ESR). The values for these properties are shown in Table II.

TABLE II. KEY ELECTRICAL PROPERTIES OF SUPERCAPACITORS CONNECTED IN SERIES

Number of SCs	Initial Voltage (V)	Overall Capacitance (mF)	Equivalent Series Resistance ( $\Omega$ )
1	1.2	170	7.5
2	2.4	85	15
3	3.55	60	22

All four IVI systems were activated using two and three SCs connected in series. The transmittance across the IVIs and the voltage across the SCs were recorded simultaneously. The results are shown in Fig. 3. When the SCs are connected in series with the IVIs, if the  $E_0$  of the SC is greater than the  $E_a$  of the IVI then the in-situ-polymerization will begin. The film forming process will proceed as the SC module discharges until the voltage of the module drops below the  $E_a$  of the IVI. At this point, the potential is too low to oxidize further monomers within the IVI and feed the electropolymerization reaction.

While both two and three SCs in series have a high enough  $E_0$  to begin the activation with the EDOT, since the CE of EDOT is so low,  $9 \text{ cm}^2/\text{C}$ , three SCs in series are required to fully activate the IVI with  $\Delta T > 80 \%$ . When only two SCs are used, a  $\Delta T$  of only 55 % is achieved. BiThiophene likewise shows full activation with three SCs, but only a  $\Delta T$  of 33 % when two SCs are used. BiEDOT and TerThiophene can be fully activated with both two and three SCs in series.

For all the monomer systems tested, faster activation is observed with three SCs than with two SCs, as the speed is dependent on the voltage. The transmittance data for activation with a 3 V coin-cell battery is also shown in Fig. 3, as this would be an alternative to SCs and light harvesting modules in a label.

#### IV. CONCLUSION

Overall, this study finds that IVIs based on in-situ polymerization can be effectively activated by printed SCs – showing potential for use in the emerging smart label market. This study shows that the contrast, as measured by  $\Delta \%T$ , and the activation speed can be modified by the selection of monomer system used in the IVI, as well as the number of SCs connected in series. BiEDOT and TerThiophene IVI systems are particularly promising systems due to their low  $E_a$ , and high CE during electropolymerization, however additional studies should be conducted to determine whether this has a detrimental impact on the long-term stability of the indicator. This system can be further optimized by modification of the IVI working area size and monomer concentration, and future work will include integration of these elements with a thermal sensor and an energy storage system on a flexible substrate as a prototype for use in the cold-chain market.

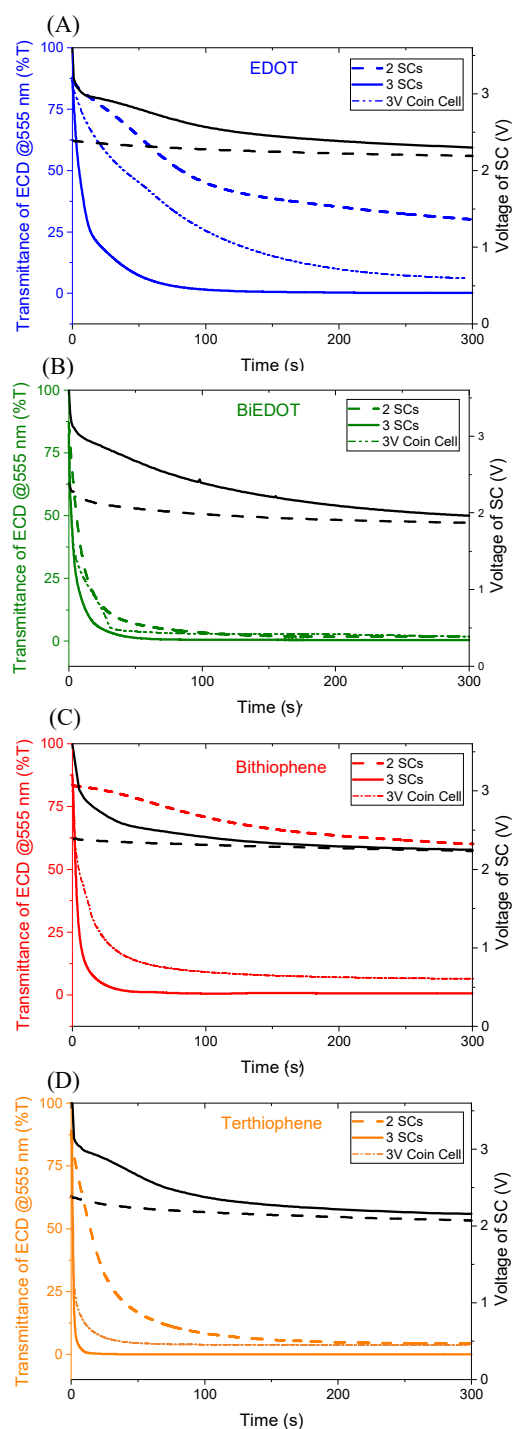


Fig. 3. Transmittance of IVIs during activation with two SCs, three SCs and a 3 V coin-cell battery for (A) EDOT, (B) BiEDOT, (C) BiThiophene, and (D) TerThiophene. Right y-axis shows the voltage of the SCs during activation. The black straight lines and the black dashed lines show the voltage of three and two series-connected SCs during activation, respectively.

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