Design equations for complementary electrochromic devices: 
application to the tungsten oxide–Prussian blue system

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Abstract

Complementary electrochromic devices (ECDs) have advantages in offering deeper switching over single-layer ECDs. Therefore, it is important to gain an insight into the dominant factors that control the electrochromic performance of complementary ECDs. In this study, the design of complementary ECDs with two reversible redox electrodes operating in series is presented. By combining the electrochemical and optical properties of these two electrodes, design equations suitable for complementary ECDs are derived. As the overall extent of electrochromic reaction involved in an ECD is limited by the electrode with a lower charge capacity, the effect of charge capacity ratio on the optical attenuation range can be predicted. The required parameters in the design equations are evaluated from the fabricated cell. As an example, the tungsten oxide–Prussian blue system is discussed. The empirical prediction of the optical attenuation range is fitted well with the experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Charge capacity; Electrochromic; Optical attenuation; Prussian blue; Tungsten trioxide

1. Nomenclature

\[ A \] active electrode area (cm\(^2\))
\[ k_i \] proportionality constant defined in Eq. (10) (C/cm\(^2\))
\[ Q \] charge injected/extracted (C)
\[ q \] charge injected/extracted per unit electrode area (C/cm\(^2\))
\[ R \] charge capacity ratio (dimensionless)
\[ T \] transmittance (%)

\[ \Delta T \] transmittance window (%)
\[ \phi \] combined transmittance accounting for the presence of both transparent conducting substrate and electrolyte (dimensionless)
\[ \eta(\lambda) \] coloration efficiency (cm\(^2\)/C)
\[ \eta'_i \] defined in Eq. (8) (cm\(^2\)/C)
\[ \lambda \] wavelength (nm)

Greek letters
\[ \alpha \] attenuation coefficient (cm\(^{-1}\))
\[ \alpha'_i \] defined in Eq. (12) (cm\(^2\)/C)
\[ \delta \] film thickness (cm)
\[ \Delta OD \] optical density change (dimensionless)

Superscripts
0 initial state
b bleached state
calc calculated value
d darkened state
m maximum value
res residual value
rxn reacted value

Subscripts
550 measurement performed at \( \lambda = 550 \) nm

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2. Introduction

A complementary electrochromic device is essentially a transparent electrochemical battery which consists of three major components: (1) electrochromic working electrode, (2) electrochromic counter-electrode, and (3) electrolyte. Such electrochromic devices exhibit reversibly adjustable light transmittance induced by an applied, low-voltage dc electrical current. In fact, WO3 is probably the most investigated material among various electrochromic materials [1]. Despite extensive research efforts so far, there are several problems that still need to be overcome before the realization of the device. These include the need for an electrochemically reversible, charge balanced counter-electrode and a thermally, as well as electrochemically, stable electrolyte over a wide temperature range.

2.1. Complementary electrochromic systems

Among various electrochromic materials, tungsten oxide has been investigated by many researchers and is thought to be one of the best choices for the primary working electrode material. A complementary counter-electrode colors and bleaches in phase with the working electrode material. A complementary counter-electrode, or

\[
\eta(\lambda) = \frac{Q/A}{q} \log\left(\frac{T^b}{T^d}\right)
\]

where \(M^+\) can be Li\(^+\), Na\(^+\) or K\(^+\). Itaya et al. [2] among others reported that K\(^+\) is the best of these as a counter ion for PB in aqueous electrolytes because of the small radius of its hydrated ion. While PB is an interesting counter-electrode material, it is generally known for its incompatibility with liquid proton-conducting electrolytes [3,4]. Proton hydration is believed to cause the incompatibility. Presumably, this is due to hindrance by the attached H\(_2\)O in the zeolitic PB.

2.3. Coloration efficiency

One of the most important criteria in selecting an electrochromic material is its coloration efficiency. The coloration efficiency of the electrochromic material \(i\), \(\eta_i(\lambda)\), is defined as the change in optical density (at a particular wavelength) per unit of injected charge density, or

\[
\eta_i(\lambda) = \frac{\Delta OD(\lambda)}{Q/A} = \frac{\log\left(\frac{T^b}{T^d}\right)}{q}
\]

where \(\Delta OD(\lambda)\) is the optical density change measured at wavelength \(\lambda\), \(Q\) the amount of charge injected/extracted, \(A\) the active electrode area, \(T^b\) and \(T^d\) the transmittances at \(\lambda\) in the bleached and darkened state, respectively, and \(q\) the charge injected/extracted per unit electrode area. It can be shown that the overall coloration efficiency of a complementary electrochromic system, \(\eta(\lambda)\), is the sum of the coloration efficiencies of the individual coloring films. That is, the overall coloration efficiency is the sum of the coloration efficiency of the working electrode and that of the counter-electrode, or

\[
\eta(\lambda) = \eta_w(\lambda) + \eta_c(\lambda) = \frac{\Delta OD(\lambda)}{Q/A}_w + \frac{\Delta OD(\lambda)}{Q/A}_c
\]

A partial list of complementary ECDs containing the WO\(_3\)–PB couple explored during the past two decades is summarized in Table 1, including transmittance values for each system where known.

It is noted, from Table 1, that complementary electrochromic devices made with the WO\(_3\)–PB couple, when in conjunction with a Li\(^+\), K\(^+\), or H\(^+\)-conducting electrolyte, are generally known to have low bleached state transmittance. Among all ECDs summarized in Table 1, Kase et al. [14,15] reported a device based on the WO\(_3\)–PB couple by using a 1 M LiClO\(_4\) in propylene carbonate with 1–2% H\(_2\)O as the electrolyte. Typical luminous transmittances in the darkened state were 5–10% while those of the bleached state were 50–70%. However, the variation of the transmittances, both in the darkened and the bleached states, is unclear. Although many researchers have reported about the transmittance range for prospective configurations, as shown in Table 1, nevertheless, very little information about the theoretical modeling for the transmittance is available for analysis.
In an earlier report [17], we found that the variation of the transmittance range depends both on the size of the sample and on the charge capacity ratio on two electrodes. In the present study, as a means of enhancing the proton compatibility with PB electrode and of varying the charge capacity ratio on two electrodes, $H_xWO_3$ proton-conducting solid polymer electrolyte ($H^+$/SPE)/PB complementary cells were made. This electrochromic transparency configuration, of electrically conductive glass/$H_xWO_3$/H$^+$-SPE/PB; electrically conductive glass, hereafter referred to as $H_xWO_3$/H$^+$-SPE/PB, is based on the complementary electrochemistry of Eqs. (1) and (2) with $M^+$ being $H^+$. It is shown, both theoretically and experimentally, that the key to approaching the optimal transmittance attenuation lies in the ability to maintain balanced charge capacity between the working and the counter-electrodes. That is, the best performing complementary electrochromic device possesses nearly ideally matched charge capacities.

![Fig. 1. Schematic representation describing the electrode’s charge capacity in partially pre-darkened and completely pre-darkened conditions.](image)

Fig. 1. Schematic representation describing the electrode’s charge capacity in partially pre-darkened and completely pre-darkened conditions.

In this paper, the cell configuration of $H_xWO_3$/H$^+$-SPE/PB is fabricated in which the H$^+$-SPE is based on the copolymer of sodium vinylsulfonic acid (Na$^{+-}$VSA) and 1-vinyl-2-pyrrolidinone (VP) [18–20]. This class of copolymer electrolytes, when synthesized with an appropriate molar ratio of comonomer, is stable at temperatures as high as 90°C, continuously for over a month [19].

### 3. Model development

In this section, the transmittance of a complementary ECD will be related to the electrochemical and optical properties of each coated electrochromic layer (EC layer). In the following derivation, we will present transmittance functions for the current system, $H_xWO_3$/H$^+$-SPE/PB. However, it is apparent that the use of the equation is valid for all complementary ECDs.

#### 3.1. Conservation of charge

It is a common practice that EC films have to be pre-colored before assembling into a complementary ECD. Fig. 1 is a schematic representation describing the electrode’s charge capacity in partially pre-darkened and completely pre-darkened conditions. The conservation of charge on the $i$th EC layer gives

$$q^{\text{res}}_i = q^0_i - q^{\text{res}}_i$$

#### Table 1

Examples of complementary ECDs containing the WO$_3$–PB couple

<table>
<thead>
<tr>
<th>Configurations</th>
<th>$T$ (%)</th>
<th>$\lambda$ (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_xWO_3/H_3PO_4$ –KH$_2$PO$_4$ in PVA/PB</td>
<td>$12 \approx 52$</td>
<td>690</td>
<td>[8]</td>
</tr>
<tr>
<td>$Li_xWO_3/Li^+$ –OMPE/PB</td>
<td>$32 \approx 63$</td>
<td>790</td>
<td>[9]</td>
</tr>
<tr>
<td>$Li_xWO_3/LiCF_3SO_3$ in PAA–PEO/PB</td>
<td>$10 \approx 60$</td>
<td>Vis</td>
<td>[10]</td>
</tr>
<tr>
<td>$Li_xWO_3/LiClO_4$ in PEO/PC</td>
<td>$5–10 \approx 50$</td>
<td>Vis</td>
<td>[11–13]</td>
</tr>
<tr>
<td>$Li_xWO_3/LiClO_4$ in PC/PO/PC</td>
<td>$5–10 \approx 70$</td>
<td>–</td>
<td>[14,15]</td>
</tr>
<tr>
<td>$H_xWO_3/\text{Poly}$ –AMPS/PC</td>
<td>$3 \approx 55$</td>
<td>550</td>
<td>[16]</td>
</tr>
<tr>
<td>$H_xWO_3/P(\text{VSA–VP})$ /PB</td>
<td>$3–6 \approx 62$</td>
<td>550</td>
<td>[17]</td>
</tr>
<tr>
<td>$H_xWO_3/P(\text{VSA–VP})$ /PB</td>
<td>$4–13 \approx 43$</td>
<td>550</td>
<td>This work</td>
</tr>
</tbody>
</table>

$a$ (OMPE = oxyethylene poly(oxyethylene); PAA = poly(acrylic acid); PC = propylene carbonate; PEO = poly(ethylene oxide); poly-AMPS = poly(2-acrylamido-2-methylpropene sulfonic acid); PU = polyurethane; PVA = poly(vinyl alcohol); P(VSA–VP) = copolymer of vinylsulfonic acid and 1-vinyl-2-pyrrolidinone; VP = 1-vinyl-2-pyrrolidinone; VSA = vinylsulfonic acid)

$b$ AMPS is a registered trademark of Lubrizol Corporation.
where \( q_i^0 \), \( q_i^{\text{res}} \), and \( q_i^{\text{res}} \) represent the initial, reacted, and residual charge capacity of the \( i \)th EC layer, respectively. Therefore, Eq. (3) can be put into the following form

\[
\eta_i(\lambda) = \left[ \frac{\Delta \text{OD}_i(\lambda)}{q_i^0} \right] = \left[ \frac{\log(T_i^h/T_i^d)}{q_i^0} \right] = \left[ \frac{\log(T_i^h/T_i^d)}{q_i^{\text{res}}} \right]
\]  

(6)

or

\[
T_i = T_i^d \exp[-\eta_i(q_i^0 - q_i^{\text{res}})]
\]  

(7)

where

\[
\eta_i = 2.303 \eta_i
\]  

(8)

The transmittance of the \( i \)th EC layer in the bleached state, \( T_i^h \), can be expressed as

\[
T_i^h = \exp(-\alpha_i \delta_i)
\]  

(9)

where \( \alpha_i \) and \( \delta_i \) represent the attenuation coefficient and the film thickness of the \( i \)th EC layer, respectively. Since the maximum charge capacity of the \( i \)th EC film, \( q_i^{\text{m}} \), is proportional to its thickness, \( \delta_i \), i.e.

\[
q_i^{\text{m}} = k_i \delta_i
\]  

(10)

where \( k_i \) is the proportionality constant, Eq. (9) becomes

\[
T_i^h = \exp(-\alpha_i q_i^{\text{m}})
\]  

(11)

where

\[
\alpha_i = \alpha_i/k_i
\]  

(12)

The transmittance of the \( i \)th EC layer can be related to its physical properties and its residual charge capacity according to

\[
T_i(q_i^{\text{m}}, q_i^{\text{res}}) = \exp(-\alpha_i q_i^{\text{m}}) \exp[-\eta_i(q_i^0 - q_i^{\text{res}})]
\]  

(13)

### 3.2. Transmittance functions

Taking the complementary H\(_2\)WO\(_4\)/H\(^+\)-SPE/PB system as an example, the overall transmittance of the device is the multipliers of the transmittance of each component. That is, the transmittance of the ECD can be formulated by the following expression

\[
T_{ECD} = \phi T_p T_w
\]  

(14)

where \( T_{ECD} \), \( T_p \), and \( T_w \) represent the transmittances of ECD, PB, and WO\(_3\), respectively. \( \phi \) is the combined transmittance accounting for the presence of both transparent conducting substrate and SPE. From Eq. (13), the transmittances of electrochromic Prussian blue and tungsten oxide can be written as

\[
T_p = \exp(-\alpha_p q_p^{\text{m}}) \exp[-\eta_p(q_p^0 - q_p^{\text{res}})]
\]  

(15)

and

\[
T_w = \exp(-\alpha_w q_w^{\text{m}}) \exp[-\eta_w(q_w^0 - q_w^{\text{res}})]
\]  

(16)

Notice that

\[
q^{\text{res}} = q_p^{\text{res}} = q_w^{\text{res}}
\]  

(17)

Assuming that both the conducting substrate and SPE are transparent (\( \phi = 1 \)), the transmittance of the ECD is

\[
T_{ECD}^w = T_{ECD}^m \exp[-\eta_p(q_p^0 - q_p^{\text{res}}) - \eta_w(q_w^0 - q_w^{\text{res}})]
\]  

(18)

where

\[
T_{ECD}^m = \exp[-(\alpha_p q_p^{\text{m}} + \alpha_w q_w^{\text{m}})]
\]  

(19)

### 3.3. Charge capacity ratio and limiting electrode

Let us define the charge capacity ratio, \( R \), as the initial charge capacity of WO\(_3\) to that of PB, i.e.

\[
R = q_w^0/q_p^0
\]  

(20)

On the basis of our previous study on complementary ECDs [21,22], it was found that the electrode with a lower charge capacity would determine the amount of charge consumed per unit area when switching occurs. The electrode with a lower charge capacity is usually called the limiting electrode. In fact, the concept of the limiting electrode can be understood both experimentally [21] and theoretically [22] by comparing the cyclic voltammetries for cells made with various charge capacity ratios. The concept of the limiting electrode, indeed, is expected by considering the general charge limitation model in a complementary electrochromic system as proposed by Rauh and Cogan [23]. Therefore, the charge consumed per unit area in a complementary ECD, \( q^{\text{res}} \), can be expressed by the following equation

\[
q^{\text{res}} = \text{Min}(q_p^0, q_w^0)
\]  

(21)

### 3.4. Transmittance window

In the case when \( 0 \leq R \leq 1 \), \( q_w^0 \leq q_p^0 \), the final bleached state and the initial darkened state transmittances, \( T_{ECD}^b \) and \( T_{ECD}^d \), of the device can be obtained from Eq. (18) by setting \( q^{\text{res}} = q_p^0 \) and \( q^{\text{res}} = 0 \), respectively. That is

\[
T_{ECD}^b = T_{ECD}^m \exp[-\eta_p q_p^0(1 - R)]
\]  

(22)

and

\[
T_{ECD}^d = T_{ECD}^m \exp[-q_p^0(\eta_p + \eta_w R)]
\]  

(23)

The transmittance window for \( 0 \leq R \leq 1 \), \( \Delta T_{ECD}(0 \leq R \leq 1) \), is obtained by subtracting Eq. (23) from Eq. (22)

\[
\Delta T_{ECD}(0 \leq R \leq 1) = T_{ECD}^m [\exp[-\eta_p q_p^0(1 - R)] - \exp[-q_p^0(\eta_p + \eta_w R)]]
\]  

(24)
Similarly, when \( R \geq 1, ( q^w_0 \geq q^b_0 ) \), the final bleached state and the initial darkened state transmittances, \( T^b_{\text{ECD}} \) and \( T^w_{\text{ECD}} \), of the device can be obtained from Eq. (18) by setting \( q^{rm} = q^w_0 \) and \( q^{rm} = 0 \), respectively. That is

\[
T^b_{\text{ECD}} = T^w_{\text{ECD}} \exp[- \eta_+ q^0_0 (R - 1)]
\]  

and as in Eq. (23) the transmittance window for \( R \geq 1 \), \( \Delta T_{\text{ECD}}(R \geq 1) \), is obtained by subtracting Eq. (23) from Eq. (25)

\[
\Delta T_{\text{ECD}}(R \geq 1) = T^b_{\text{ECD}} \exp[- \eta_+ q^0_0 (R - 1)] - \exp[- q^0_0 (\eta_+ + \eta_- R)]
\]

4. Experimental

4.1. WO₃ working electrode

The experimental procedures for the preparation of WO₃ have been described elsewhere [24]. WO₃ was vacuum-deposited on fluorine-doped tin oxide (FTO)-coated glass substrates. The sheet resistance of FTO-coated glass substrates was measured by the four-point probe method and was 10 \( \Omega \). Conductive copper bus bars were applied on all four sides of the FTO-coated substrate. FTO-coated glass substrates were coated in copolymer solution in aqueous cleaner solution reported previously [24,25]. Tungsten oxide films prepared in this way had a thickness of 370 ± 50 nm. X-ray diffraction analysis, with a Rigaku diffractometer (Model D-2655) using monochromatized Cu Kα incident radiation, showed all the films to be lacking crystallinity.

4.2. PB counter-electrode

The sacrificial anode method, which is based on the cathodic electrodeposition mentioned by Ellis et al. [26] for PB deposition, was modified and used in this work. The modified sacrificial method for PB deposition was described elsewhere [27]. The solution contained 5 mM of FeCl₃·6H₂O and 5 mM of K₃Fe(CN)₆. It takes about 30 min to deposit the desired amount of PB on FTO-coated glass. The thickness of the PB film was controlled at 475 ± 25 nm by counting the passed charge, which is proportional to the amount of PB deposited. In all cases, the charge capacity for the deposition was controlled at 13.2 mC/cm². X-ray diffraction analysis, with a Rigaku diffractometer (Model D-2655), using monochromatized Cu Kα incident radiation, showed all the films to be crystalline.

4.3. Solid polymer electrolyte

The transparent electrolyte is the copolymer based on the copolymerization of Na⁺-VSA and VP [18]. The sodium form of this copolymer is exchanged to the acid form for use as the electrolyte in electrochromic devices. Na⁺-VSA/VP copolymerization is intentionally done with a slightly enriched VP than desired: 1.6:1 Na⁺-VSA/VP to obtain 2:1 poly(Na⁺-VSA/VP) copolymer, for example. The experimental details for the preparation of the copolymer were described elsewhere [19].

4.4. Cell assembly

Before assembling the cells, the WO₃ electrode was pre-charged with protons. A constant current density of 0.11 mA/cm² was used in cathodizing the tungsten oxide electrode. It takes about 4 min to get the pre-determined amount of protons, which will be described in Section 4, into the tungsten oxide thin film. The tungsten bronze, H₃WO₃, was then rinsed with distilled water and dried under N₂. The polymer electrolyte was flow-coated on both electrodes. Conditioning was done in a room with a controlled relative humidity of 35% at 23°C. Cells were intimately laminated together with H₃WO₃ as the working electrode and PB as the counter-electrode. The lamination was carried out in an autoclave at a pressure of 1.03 \times 10⁶ N/m² and a temperature of 93°C for 1 h [28]. This procedure resulted in an averaged thickness of 100 μm for the copolymer electrolyte, as measured by a micrometer across the samples. After autoclaving, each cell was sealed around all four edges with butyl rubber. The electroactive areas of the ECD was 10.2 × 15.2 cm².

4.5. Electrochemical runs

The coloration and bleaching of cells were carried out by applying a constant dc voltage (Keithley voltage/current source, Model 228A). The transmittance, current and drift of the cell voltage were recorded. The change in optical transmittance during coloration and bleaching was measured at 550 nm with a Cary-14 spectrophotometer. Transmittance data were taken at or near the center of each cell, depending on the size of the sample.

5. Results and discussion

5.1. Electrochromic performance

Five ECDs, each with different charge capacity ratios, were made. WO₃ electrodes (active area = 10.2 × 15.2 cm²) were pre-charged in copolymer solution in order to optimize the pre-charging conditions, to match
Table 2
Electrochromic samples made with different $R$ values switched at $1.2$ and $0.6$ V

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R$</th>
<th>$T_{550}$ (%)</th>
<th>$\Delta T$ (%)</th>
<th>$\Delta OD$</th>
<th>$q^{\text{rxn}}$ (mC/cm$^2$)</th>
<th>$\eta$ (cm$^2$/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0.66</td>
<td>12.0 ± 53.0</td>
<td>41.0</td>
<td>0.65</td>
<td>11.36</td>
<td>56.8</td>
</tr>
<tr>
<td>S-2</td>
<td>0.82</td>
<td>13.0 ± 62.5</td>
<td>49.5</td>
<td>0.68</td>
<td>12.72</td>
<td>53.6</td>
</tr>
<tr>
<td>S-3</td>
<td>1.15</td>
<td>6.6 ± 70.2</td>
<td>63.6</td>
<td>1.03</td>
<td>20.00</td>
<td>51.3</td>
</tr>
<tr>
<td>S-4</td>
<td>1.32</td>
<td>5.2 ± 57.4</td>
<td>52.2</td>
<td>1.04</td>
<td>19.03</td>
<td>54.8</td>
</tr>
<tr>
<td>S-5</td>
<td>1.48</td>
<td>3.9 ± 43.0</td>
<td>39.1</td>
<td>1.04</td>
<td>17.79</td>
<td>58.6</td>
</tr>
</tbody>
</table>

5.3. Transmittance vs. charge capacity ratio

The data points in Fig. 3 indicate the bleached and darkened state transmittances measured at 550 nm, which are designated by $T_{\text{ECD}}^b$ and $T_{\text{ECD}}^d$, respectively, against the ratio of charge capacity, $R$, of the H$_x$WO$_3$ to that of the PB, $R = q_0^w/q_0^p$. Both the darkened and the bleached state transmittances were fitted very well with the model, as revealed by the modeling curves by choosing $T_{\text{ECD}}^b = 0.8$ and $\eta_p^b = \eta_w^b$.

The experimental data shown in Fig. 4 are the transmittance window measured at 550 nm, $\Delta T_{\text{ECD}} = T_{\text{ECD}}^b - T_{\text{ECD}}^d$, against the ratio of charge capacity, $R$. It was interesting to find experimentally that the closer the ratio of two charge capacities to unity ($R \approx 1.0$), the wider the transmittance window or attenuation. In fact, the theoretical model predicts the experimental results very well, as shown by the curve in Fig. 4.

5.2. Charge consumption

Fig. 2 shows the charge consumed per unit area as a function of the charge capacity ratio. The experimental data are shown by the diamond points while the model prediction is shown by the solid line based on the measured value of $q_0^w = 21.61$ mC/cm$^2$. The dotted line is the best fit to the model with a value of $q_0^{\text{calc}} = 17.91$ mC/cm$^2$, which is 17% smaller than the measured value. The discrepancy in $q_0^{\text{rxn}}$ is due to the partial oxidation of the H$_x$WO$_3$ electrode, in the presence of O$_2$ in the electrolyte [17], through Eq. (27)

$$H_xWO_3 \cdot mH_2O + \frac{x}{4}O_2 \rightarrow WO_3 \left( m + \frac{x}{2} \right)H_2O.$$  (27)
Fig. 3. Bleached and darkened state transmittances at 550 nm as a function of the charge capacity ratio. The experimental data are shown by the diamond points while the model predictions are shown by the curves with $T_{\text{ECD}}^0 = 0.8$ and $\eta_p^0 = \eta_w^0$. The active area of the ECD is 155.0 cm$^2$.

6. Conclusions

This study deals with balancing the electrode capacities in a complementary, solid-state electrochromic device so as to optimize its optical attenuation. This work outlines the combined electrochemical and optical design equations for complementary ECDs with application to the solid-state electrochromic configuration of $\text{H}_x\text{WO}_3/\text{H}^+\cdot\text{SPE}/\text{PB}$. The present research provides a simple engineering guideline for designing the complementary ECDs. It will also help in better understanding the key factors that govern the performance of complementary ECDs. The main conclusions from this study are:

1. The concept of the limiting electrode is verified experimentally for complementary ECDs by observing $q_{\text{rxn}}^{\text{min}}(q_p^0, q_w^0)$.
2. The matching of two charge capacities in a complementary ECD was confirmed experimentally by showing that the closer the ratio of the two charge capacities to unity ($R \rightarrow 1.0$), the wider the transmittance window.
3. By combining the electrochemical and optical properties of these two electrodes, design equations suitable for complementary ECDs are derived. These equations are fitted very well with our experimental data.
4. The principle of optimal design in obtaining the maximum optical attenuation is to equalize the charge capacity on both the EC layers.

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