Interpretations of voltammograms in a typical two-electrode cell: application to complementary electrochromic systems

Lin-Chi Chen, Kuo-Chuan Ho *

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Received 21 August 2000; received in revised form 7 November 2000

Abstract

Most electrochemical measurements and characterizations rely on a three-electrode system to obtain useful information. Nevertheless, useful information can still be obtained with a two-electrode system when electrochemical measurements done with a three-electrode system become difficult or impossible. For example, cyclic voltammetry performing on an electrochromic device (ECD) at low scanning rates was proposed as a means to determine the limits of the safe operating voltage. In this study, voltammograms in a typical two-electrode cell is simulated digitally. It was found from the numerical simulation that the voltammograms of the cell could provide ‘fingerprints’ of an ECD. These fingerprints agree well with our earlier experimental observation that the cell characteristics are governed by the electrode with a lower charge capacity. To illustrate the validity of the simulation, complementary electrochromic system comprising the tungsten oxide–polyaniline pair will be discussed. Useful criteria for cell design are also presented. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Charge capacity; Electrochromic; Polyaniline; Tungsten trioxide; Two-electrode voltammetry

1. Introduction

Cyclic voltammetry has proven to be a powerful diagnostic tool for characterizing many electrochemical systems, including electrochromic materials and devices. In this work, unlike common voltammetry relying on a three-electrode system [1], a two-electrode issue is evolved. Voltammograms in a typical two-electrode cell have been interpreted. Although the use of controlled-potential technique in a two-electrode cell has been limited to certain electrochemical systems due to the accompanied counterelectrode’s polarization [2], the technique still plays a very important role in characterizing a well-sealed electrochemical cell such as a complementary electrochromic device (ECD), and it also provides much useful information. For example, Kase et al. [3] used a two-electrode voltammogram to determine the driving voltage of a WO$_3$/Prussian blue (PB) ECD; similarly, we also took advantage of the same technique to seek the safe operating voltages of WO$_3$/polyaniline (PAni) electrochromic systems in our previous work [4]. Schmitt and Aegerter [5] employed this method to compare ECDs made with Nb$_2$O$_5$ and Nb$_2$O$_5$:X (X = Li, Ti, Mo) as colouring electrodes. Besides, two-electrode voltammetry can also be applied to characterize other electrochemical devices, like light-emitting electrochemical cells [6,7] and secondary batteries. Furthermore, Wightman [8] and Bruckenstein [9] even recommended the use of the two-electrode system for which the resistance between working and counter electrodes can be easily determined and compensated.

When an electrochemical system is chosen properly, the two-electrode potential-sweep method can provide much needed information by characterizing electrochemical performances of a cell; however, if it is not
done properly, this technique is not robust and may lead to poor reproducibility making the comparison meaningless. For instance, Jelle et al. [10,11] and Bernard et al. [12] worked on a very similar tungsten oxide–polyaniline electrochromic system comprising the same electrodes and the same ioni-
cally conducting polymer electrolytes; however, the voltammograms obtained were quite different. Thus, before applying the two-electrode technique, it would be better for researchers to realize what factors influence the voltammogram in a typical cell and how to obtain a reproducible voltammogram.

A two-electrode voltammogram is often assumed to be dependent on scanning rates, component electrodes kinetic behaviours, oxidation states, and some undesirable cell properties such as uncompensated resistances and capacitances; however, a key point to determine what a cell’s voltammogram looks like was verified to be the charge capacity ratio between two component electrodes. From a recent study on the WO3/PAni ECD, it was found that the voltammogram of the device is strongly affected by the charge capacity ratio between polyaniline and tungsten oxide [4]. Furthermore, the electrode with a lower charge capacity limits the performance of the cell. This is illustrated by comparing the device’s voltammograms (Fig. 1(c)) with the typical voltammograms of an electrodeposited PAni film (Fig. 1(a)) and a sol–gel WO3 film (Fig. 1(b)) [4]. These findings not only provide a clue to better control the reproducibility of two-electrode voltammetry, but also depict the influences of charge capacity ratio on cell performances, which has been an important issue for designing both ECDs [13–16] and lithium-ion secondary battery [17]. For example, ECDs showing different voltammograms [18], while composed of the same electrodes, may simply be the effect of having different charge capacity ratios.

To make two-electrode voltammetry a more reliable and robust technique, our aim is to understand how the charge capacity ratio affects the voltammogram in a typical two-electrode cell. As far as we know, very little literature has been devoted to this issue. Although Orlik [18] had simulated cyclic voltammograms in a two-electrode system with the rigorous mathematical treatment by considering a non-Faradaic effect, the important problem such as the polarization effect on a counterelectrode was not considered. To address this issue, one of our main concerns in this work is aimed towards the study of the influence of charge capacity ratio on the counterelectrode’s polarization.

To interpret the effect of charge capacity ratio on a cell’s voltammogram that is to be compared with Fig. 1, two electrodes, each with assumed voltammograms of its own, based on their specific thin-film electrochemistry are considered [19–23]. Moreover, by taking Kirchhoff’s current law [1] and further simplifications into account, slow-scanning voltammograms for a cell comprising the postulated electrodes with different charge capacity ratios are simulated numerically. Finally, the work not only verifies an earlier finding that the lower-capacity electrode limits a cell’s performance but also discusses thoroughly the influence of charge ratio.
A slow-scanning voltammometric response of an electrochromic thin film is often explained by the thin-film model, which accounts for the effect of mutual interactions between O and R, where \( m = 1, 1/2, 0, -1/2, \) and \(-1\).

capacity ratio on the distribution of a cell’s voltage and its operating voltage.

2. Theoretical aspect and method

2.1. Electrochemistry of electrochromic thin films

A slow-scanning voltammometric response of an electrochromic thin film is often explained by the thin-film electrochemistry [19–23]. For a typical reversible redox process, \( \text{O} + ne^- \leftrightarrow \text{R} \), occurs on a monolayer or in a thin film, the rate of the electrode reaction per area, \( I/nF \), can then be equated to the rate of reduction of \( \text{O} \) to yield \( \text{R} \) at 25°C; \( f = F/RT = 38.92 \text{ V}^{-1} \) at 25°C; \( m \) is the Margules constant, which directly reflects the excess free energy for the mixing process of \( \text{O} \) and \( \text{R} \). Simply speaking, the above formula is merely the Nernst equation but with a single parameter correction and it results in the following probability density function

\[
\frac{dx_R}{dE} = nF \left( 2m + \frac{1}{(\chi_R - 1)\chi_R} \right)^{-1}
\]

The plot of \( (dx_R/dE) \) versus \( (E - E_0) \) with different \( m \) values \( (m = 1, 1/2, 0, -1/2, \) and \(-1\) at 25°C for \( n = 1 \) is given in Fig. 2. It can be seen that the more negative the \( m \) value, the flatter the curve, with the integrated area of each probability density function equal to unity. Hence, it is believed that the voltammetric shape of a thin film is intrinsically dependent upon its corrected Nernstian expression. Briefly speaking, the curve’s shape is governed by the interaction parameter \( m \). This leads to voltammograms of different shapes among materials because of different interaction behaviours involved. In fact, this viewpoint was proposed in some classical literature with rigorous treatments by considering the lateral-interaction effects [21–23]. Laviron [22] firstly applied a Frumkin-type isotherm with a random distribution assumption and obtained the \( I-E \) behaviours similar to those presented in Fig. 2. By contrast, Matsuda et al. [23] derived a voltammetric model for an organized film and proposed an unusual double-wave voltammogram for some interaction parameters.

Fig. 2. The probability density function derived from thermodynamics of mixed-valence intercalation reactions proposed by MaCargar and Neff [26]. In the model, a film is viewed as a binary solution of \( \text{O} \) and \( \text{R} \), and \( m \) is the Margules constant to account for the effect of mutual interactions between \( \text{O} \) and \( \text{R} \), where \( m = 1, 1/2, 0, -1/2, \) and \(-1\).
2.2. Probability density functions of different shapes

To observe the shape influence of a charge capacity ratio on a cell’s voltammogram directly, we postulate two electrodes with two different probability density functions instead of the above-mentioned corrected Nernstian forms. For simplicity, one probability density function is a triangular shape as shown in Fig. 3(a) for the positive electrode; the other is a semi-ellipse as given in Fig. 3(b) for the negative electrode. Referring to Fig. 2, the triangular function may be viewed as the case of $m = 1$, while the semi-elliptic function as the case of $m = -1$. In practice, the mathematical expressions for these two functions are chosen as Eqs. (4) and (5) after a thorough consideration to fulfil the characteristics of a probability density function, i.e. the integrated area of unity.

(1) For the positive electrode with a triangular probability density function:

$$\frac{d\chi_p}{dE} = \begin{cases} 1 - |E - E_p| & \text{for } E_p(V) \in [0, 2] \\ 0 & \text{otherwise} \end{cases}$$

(4)

$$\chi_p = \begin{cases} 1 & E_p \geq 2 \text{ V} \\ 0 & E_p \leq 0 \text{ V} \end{cases}$$

(2) For the negative electrode with a semi-elliptic probability density function:

$$\frac{d\chi_n}{dE} = \begin{cases} \frac{(2/\pi)\sqrt{1 - (E_n + 1)^2}}{10^6 \text{ mol/cm}^2} & \text{for } E_n(V) \in [-2, 0] \\ 0 & \text{otherwise} \end{cases}$$

(5)

$$\chi_n = \begin{cases} 1 & E_n \leq -2 \text{ V} \\ 0 & E_n \geq 0 \text{ V} \end{cases}$$

The superscript P denotes the positive electrode and N for the negative one. It shall be stressed here that Eq. (4) is defined as a function of $x_O$, while Eq. (5) is written for $x_R$. Since before the discharge process of a cell, a positive electrode must contain only the oxidized species; conversely, a negative one is expected to exist at a fully reduced state.

2.3. Charge capacity ratio

The charge capacity of thin film $i$, $q^i$ can be obtained by integrating its voltammetric current density, $i = I/A$ from Eq. (1). While capacities of two electrodes are measured at the same scan rate, their charge capacity ratio, $R$, is defined as follows

$$R \equiv \frac{q^P}{q^N} = \frac{\int_{E = -\infty}^{E = \infty} i^P dE}{\int_{E = -\infty}^{E = \infty} i^N dE} = \frac{n^P \Gamma_P}{n^N \Gamma_N}$$

(6)

For convenience of calculation, electron-transfer numbers $n^P$ and $n^N$ are both assumed to be 1. On the other hand, $\Gamma_P$ is fixed at $10^{-6}$ mol/cm$^2$, while $\Gamma_N$ is varied to make five different charge capacity ratios, say $R = 20, 2, 1, 0.5, 0.05$ for further simulation about the effect of the charge capacity ratio on a cell’s voltammogram.

2.4. Digital simulation for two-electrode voltammograms

Voltammograms of a cell ($i^{\text{CELL}}$ versus $V^{\text{CELL}}$) comprising the postulated electrodes (P and N) with different charge capacity ratios ($R = 20, 2, 1, 0.5, 0.05$) are simulated by the following considerations and approaches.

**Fig. 3.** (a) A postulated positive electrode with a triangular-shape probability density function. (b) A postulated negative electrode with a semi-elliptic probability density function.
2.4.3. The cell’s voltage

To simplify the simulation task, two assumptions are made. Firstly, we assume that the slow-scanning voltammetric current is small enough so as to neglect the effect of \( iR \) drops. Secondly, the facile kinetics assumption holds true, so one does not need to take overpotentials into consideration. As a result, the cell’s voltage under a cathodic sweep (a discharge process) is merely the potential difference between two electrodes. Furthermore, a slow scan rate (\( n \)) of 1 mV/s is applied to the simulated voltammetry for rationalizing the assumptions. Thus, we have

\[
V_{\text{CELL}} = E^P(x_O^P) - E^N(x_R^N) = 4 - v t = 4 - 0.001 t \quad (9)
\]

and,

\[
\frac{dV_{\text{CELL}}}{dt} = \frac{dE^P}{dt} - \frac{dE^N}{dt} = - v = - 0.001 \quad (10)
\]

In fact, Eq. (9) was utilized to determine the safe operating voltages for a complementary ECD by Rauh and Cogan [14]. Eqs. (9) and (10) revealed that neither the potential of the working electrode nor counter electrode is well controlled, when performing the two-electrode voltammetry to a cell; instead, all we control is the cell’s voltage, \( V_{\text{CELL}} \), alone.

2.4.4. Numerical approach and digital simulation

Broadly speaking, to simulate a cell’s voltammogram is to mainly solve Eqs. (7) and (9) along with the initial condition. Since the mathematics involved is non-linear in nature, voltammograms are simulated numerically. The numerical approach to be adopted is the explicit finite difference method [24], and a FORTRAN90 routine is built to complete the numerical work. All calculations are executed by a personal computer with an Intel Pentium-S CPU at 200 MHz. To sum up, \( i_{\text{CELL}}(t) \), \( V_{\text{CELL}}(t) \), \( E^P(t) \), and \( E^N(t) \) are simulated for various charge capacity ratios from \( t = 0 \) s (\( V_{\text{CELL}} = 4 \) V) to \( t = 4000 \) s (\( V_{\text{CELL}} = 0 \) V).

3. Results and discussion

3.1. Parameters to determine the shape of a voltammogram

Simulated voltammograms (\( i_{\text{CELL}} \) versus \( V_{\text{CELL}} \)) of the cell for different charge capacity ratios (\( R \equiv q^P/q^N \)) are shown in Fig. 4. Despite the same positive and negative electrodes being used, the difference in charge capacity ratios causes the voltammograms to look very different from each other. The curves for \( R = 0.5 \) and
0.05 both exhibit a triangular feature, as seen in Fig. 3(a); on the contrary, when the ratio is larger than unity ($R = 2$ or $20$), a semicircle-like curve is approached, as seen in Fig. 3(b). Only when the charge capacity ratio is equal to 1, a mixed-shape curve is obtained. These curves reveal that the shape of a cell’s voltammogram is determined by the voltammogram ($I–E$ behaviour) of an electrode with the lower charge capacity. This simulated result is consistent with our previous observation on a WO$_3$/PAni ECD, as shown in Fig. 1(c). It is therefore inferred that the shape effect, as seen in both Fig. 4 (the simulated voltammograms) and Fig. 1(c) (the real ones), can be attributed to the same reason, the Kirchhoff’s current law, as outlined by Eq. (7).

According to Eq. (7), when the lower-capacity electrode runs out and contributes no currents, i.e. $x_j = 0$ ($i = O$ or $R$; $j = P$ or $N$), the larger-capacity side must terminate its redox reaction to maintain the current’s continuity. As a result, the lower-capacity electrode limits the cell’s voltammetric response and dominates the voltammogram’s shape. For this reason, to compare voltammograms for cells made of the same cathodic and anodic materials, one needs to consider the simple effect of charge capacity ratio. For example, three very different $I–V$ behaviours, a PAni-like [10], a WO$_3$-like [11], and a mixed-featured [12] voltammogram, were reported, all for very similar WO$_3$/PAni ECDs. This can be explained by the charge capacities between WO$_3$ and PAni, namely, $q_{\text{WO}_3}^\text{CELL} > q_{\text{PAni}}^\text{CELL}$, $q_{\text{WO}_3}^\text{CELL} < q_{\text{PAni}}^\text{CELL}$, and $q_{\text{WO}_3}^\text{CELL} = q_{\text{PAni}}^\text{CELL}$.

### 3.2. The limiting electrode in a two-electrode cell

Fig. 4 suggests that the lower-capacity electrode dominates a cell’s voltammogram due to the constraint of current’s continuity. This principle also implies that the lower-capacity electrode must play a limiting role in the charge/discharge process of a cell. Thus, to further prove the existence of the limiting electrode in a cell, a relationship between the maximum cell-discharge capacity, $q_{\text{CELL}}^\text{MAX}$, and the charge capacity ratio is shown in Fig. 5, which is obtained by integrating Fig. 4 against time. It is found that the maximum discharge capacity of the cell increases linearly with the capacity ratio when $R < 1$; by contrast, when $R \geq 1$, it arrives at a ceiling value, $9.65 \times 10^4 \mu\text{C/cm}^2$. As a consequence, the $q_{\text{CELL}}^\text{MAX}$–$R$ relationship can be formulated by the following equation

$$q_{\text{CELL}}^\text{MAX} = \text{Min}(9.65 \times 10^4 \times R, 9.65 \times 10^4)$$

Since we have set $\Gamma_0^w = 10^{-6} \text{mol/cm}^2$ and defined $R \equiv q_{\text{P}}/q_{\text{N}}$, clearly, Eq. (11) states that the maximum discharge capacity of the cell is equal to the charge capacity of the lower-capacity electrode. That is,

$$q_{\text{CELL}}^\text{MAX} = \text{Min}(q_{\text{P}}, q_{\text{N}})$$

Thus, the lower-capacity electrode is the limiting electrode, which not only dominates a cell’s voltammogram but also limits a cell’s Faradaic characteristics. This is against the common wisdom that the electrode with a larger capacity shall dominate a cell’s performance. Accordingly, Eq. (12) provides a thumb rule for maximizing the utilization of electrodes, that is, to maximize the utilization of cathode and anode, one needs to equalize charge capacity on both electrodes.

Concerning related experimental data to support the rule; evidences can be found in our previous works [4,16] for complementary systems of WO$_3$/PAni and WO$_3$/PB couples.

### 3.3. Distribution of a cell’s voltage between two electrodes

Since the polarization effect at the counter electrode cannot be ignored while performing the two-electrode voltammetry, the distribution of a cell’s voltage between two electrodes is still another important issue in this work. For this reason, the potentials of two component electrodes in Eq. (9), $E^\text{N}(t)$ and $E^\text{P}(t)$, are also calculated during the cell’s voltammetric simulation.

A plot of $E^\text{N}(t)$ versus $E^\text{P}(t)$ for different capacity ratios is shown in Fig. 6. The plot reveals that the distribution of a cell’s voltage is strongly influenced by the charge capacity ratio. The applied potential is not equally distributed on two-electrodes, even for the case of $R = 1$. (Unless a cell is composed of two electrodes with the same $I–E$ behaviour.)
3.4. The operating voltages of a cell

In principle, a cell shall be operated in a voltage window corresponding to the non-zero current region in its \(i-V\) curve; hence, we define a voltage window (\(\Delta V_{\text{CELL}}\)) of a cell as the cell’s voltage difference between the initial stage voltage (\(V_{\text{CELL}}^0\)) and the cutoff stage voltage (\(V_{\text{cut}}^\text{CELL}\)). The cutoff voltage is the voltage at which the voltammetric response decays to zero. By this definition, Fig. 4 not only tells how a charge capacity ratio affects the shape of a cell’s voltammogram, but also depicts the effect of a capacity ratio on a cell’s voltage window. It shows that a relatively high voltage with a narrow voltage window tends to be obtained as \(|q^p - q^N|\) gets larger. For example, the non-zero voltammetric current is ranged from 4 to 0 V and peaks at 2 V for \(R = 1\); in comparison, the voltammogram for \(R = 0.5\) peaks at ca. 2.4 V and has a voltage ranging from 4 to 1 V.

To arrive at a mathematical expression for the relationship between \(\Delta V_{\text{CELL}}\) and \(R\), Eq. (9) is re-written in terms of \(q^f\) (\(f = P\) or \(N\)) based on the principle of current continuity

\[
V_{\text{CELL}} = E^P(\chi^p_0 = \frac{q^p - q^\text{Rxn}}{q^p}) - E^N(\chi^N_0 = \frac{q^N - q^\text{Rxn}}{q^N})
\]

(13)

where \(q^\text{Rxn}\) is the reacted charge capacity during the cathodic sweep. Because \(V_{\text{CELL}}^f\) (where \(q^\text{Rxn} = 0\)) has been given as 4 V for the fully pre-polarized electrodes, \(\Delta V_{\text{CELL}}\) can be determined after calculating \(V_{\text{cut}}^\text{CELL}\). In fact, \(V_{\text{CELL}}^\text{cut}\) is the voltage at which \(q^\text{Rxn} = q^\text{CELL}\). As a result, by applying Eqs. (6) and (12) to Eq. (13) we have

\[
V_{\text{CELL}}^\text{cut} = E^P(0) - E^N(1 - R) = -E^N(1 - R)
\]

for \(q^P \leq q^N; R \leq 1\)

\[
V_{\text{CELL}}^\text{cut} = E^P(1 - R^{-1}) - E^N(0) = E^P(1 - R^{-1})
\]

(14)

for \(q^P \geq q^N; R \geq 1\)

Based on the definition of \(\Delta V_{\text{CELL}}\), the relationship between \(\Delta V_{\text{CELL}}\) and \(R\) is given correspondingly.

\[
\Delta V_{\text{CELL}} = [E^P(1) - E^N(1)] - [E^P(0) - E^N(1 - R)]
\]

\[= 4 + E^N(1 - R) \quad (R \leq 1)\]

(16)

\[
\Delta V_{\text{CELL}} = [E^P(1) - E^N(1)] - [E^P(1 - R^{-1}) - E^N(0)]
\]

\[= 4 - E^P(1 - R^{-1}) \quad (R \geq 1)\]

(17)

Finally, applying Eqs. (4) and (5) to Eqs. (14)–(17), shows why a higher voltage with a narrower voltage window tends to be obtained with \(R\)-values deviated far from unity. These equations also provide a criterion for determining operating voltages for a cell. According to the criterion, one can assemble a higher-voltage battery by enlarging the difference in charge capacity between two electrodes. Nonetheless, one needs to remember that the criterion is valid only when applied to cells composed of the fully pre-polarized electrodes with pseudo-equilibrium behaviours.

4. Conclusions

So far, we have successfully interpreted the effects of a capacity ratio on a cell’s voltammogram and found that the simulated results are in good agreement with our previous works. To sum up, these effects are concluded as follows:

1. The lower-capacity electrode dominated the shape of a cell’s voltammogram.
2. The lower-capacity electrode also limits the maximum cell-discharge capacity.
3. The larger-capacity electrode is more difficult to be polarized than the lower-capacity one.
4. The larger the capacitance difference \((q^P - q^N)\) is, the higher the voltage, and the narrower the voltage window to be obtained.

In theory, the above results are attributed to Kirchhoff’s current law, which ensures current continuity in a cell and renders the lower-capacity electrode to limit a cell’s performance. Despite the naïve and simple \((dx / dE)\) functions to be chosen, it is inferred that the conclusions of this work have the generality and can be applied to any two-electrode cell including an ECD. Of course, one can introduce the more realistic electrode thermodynamics [25–27] or kinetics [28,29] instead of proceeding with a rigorous cell’s voltammetric simulation. In conclusion, this work provides a criterion to assign a proper charge capacity ratio, realizing a way to better control the reproducibility for a two-electrode voltammetry, and giving an insight to further studies in the related areas.

Acknowledgements

This work was sponsored by the National Research Council of the Republic of China under contract numbers NSC 87-2214-E002-034 and NSC 89-2214-E002-017.

References