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

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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_2O_5 and $\text{Nb}_2\text{O}_5\text{:X}$ ($\text{X} = \text{Li}, \text{Ti}, \text{Mo}$) 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

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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 ionically 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 WO_3/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 WO_3 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

(a) Potential (mV) vs. Ag/AgCl

(b) Potential (mV) vs. Ag/AgCl

(c) Operating voltage (mV) vs. CE

Fig. 1. (a) The typical voltammogram for an electrodeposited PAni film in 0.1 N HCl. (b) The typical voltammogram for a sol–gel WO_3 film in 0.1 N HCl. (c) Two-electrode voltammograms for $\text{WO}_3/\text{PAMPS}/\text{PAni}$ ECDs with different charge capacity ratios: $R = (q^{\text{WO}_3}/q^{\text{PAni}}) = 0.47, 0.99, 1.42, \text{ and } 1.97$. Scan rate = 50 mV/s [4].

Fig. 2. The probability density function derived from thermodynamics of mixed-valence intercalation reactions proposed by McCargar and Neff [26]. In the model, a film is viewed as a binary solution of O and R, and m is the Margules constant to account 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 voltammetric response of an electrochromic thin film is often explained by the thin-film electrochemistry [19–23]. For a typical reversible redox process, $O + ne^- \rightleftharpoons R$, occurs on a monolayer or in a thin film, the rate of the electrode reaction per area, I/nFA , can then be equated to the rate of reduction of O to yield [19]

$$\frac{I}{nFA} = -\frac{d\Gamma_O}{dt} = -v \frac{d\Gamma_O}{dE} = -v\Gamma_T \left(\frac{dx_O}{dE} \right) \quad (1)$$

or the rate of production of R to give

$$\frac{I}{nFA} = \frac{d\Gamma_R}{dt} = v \frac{d\Gamma_R}{dE} = v\Gamma_T \left(\frac{dx_R}{dE} \right) \quad (1a)$$

where $\Gamma_O + \Gamma_R = \Gamma_T$ and $x_O + x_R = 1$. The symbols Γ_i and x_i ($i = O$ or R) represent the surface concentration of i th species in the film (mol/cm^2) and its corresponding mole fraction, respectively. v and E are the scanning rate and the electrode potential, respectively. Other notations maintain their meanings in the electrochemical field. Ellis et al. [20] had also applied a very similar equation to compare the voltam-

mograms at a PB electrode. Both the Ellis model and the above equations suggest that the slow-scanning voltammetric current of a thin-film electrode is basically proportional to the (dx_O/dE) or (dx_R/dE) function, namely the mole fraction density function or the probability density function of O or R. Moreover, the function is directly determined by the Nernst expression (the $E-x$ relationship) of a thin film. As a result, the voltammetric response of a thin film can be determined, if its $E-x$ behaviour is known.

To develop a general $E-x$ expression for a thin-film electrode, thermodynamics of the mixed-valence intercalation reactions proposed by Ellis et al. [20] and McCargar and Neff [26] is taken into account. Accordingly, the $E-x$ expression, by considering the thin film as a binary solid solution of O and R, is given by the following equation

$$\begin{aligned} E - E_0 &= \frac{RT}{nF} \ln \left(\frac{a_O}{a_R} \right) = \frac{RT}{nF} \ln \left(\frac{x_O \exp(mx_R^2/RT)}{x_R \exp(mx_O^2/RT)} \right) \\ &= \frac{1}{nf} \left[m(x_R - x_O) + \ln \left(\frac{x_O}{x_R} \right) \right] \end{aligned} \quad (2)$$

where a_i ($i = O$ or R) is the activity, $f = F/RT = 38.92 \text{ V}^{-1}$ at 25°C ; m is the Margules constant, which directly reflects the excess free energy for the mixing process of O and 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

$$\left(\frac{dx_R}{dE} \right) = nf \left(2m + \frac{1}{(x_R - 1)x_R} \right)^{-1} \quad (3)$$

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.

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 charac-

teristics of a probability density function, i.e. the integrated area of unity.

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

$$\left(\frac{dx_O^P}{dE^P}\right) = \begin{cases} 1 - |E^P - 1| & \text{for } E^P(V) \in [0, 2] \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$x_O^P = \begin{cases} 1 & E^P \geq 2 \text{ V} \\ 0 & E^P \leq 0 \text{ V} \end{cases}$$

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

$$\left(\frac{dx_R^N}{dE^N}\right) = \begin{cases} (2/\pi)\sqrt{1 - (E^N + 1)^2} & \text{for } E^N(V) \in [-2, 0] \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

$$x_R^N = \begin{cases} 1 & E^N \leq -2 \text{ V} \\ 0 & E^N \geq 0 \text{ V} \end{cases}$$

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

$$R = \frac{q^P}{q^N} = \frac{\left| \int_{E=-\infty}^{E=\infty} i^P dE \right|}{\left| \int_{E=-\infty}^{E=\infty} i^N dE \right|} = \frac{n^P \Gamma_T^P}{n^N \Gamma_T^N} \quad (6)$$

For convenience of calculation, electron-transfer numbers n^P and n^N are both assumed to be 1. On the other hand, Γ_T^N is fixed at 10^{-6} mol/cm², while Γ_T^P is varied to make five different charge capacity ratios, say $R = 20, 2, 1, 0.5$, and 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^{CELL} versus V^{CELL}) comprising the postulated electrodes (P and N) with different charge capacity ratios ($R = 20, 2, 1, 0.5$, and 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.

Fig. 4. Simulated voltammograms of a cell comprising the postulated positive and negative electrodes with different charge capacity ratios ($R = 20, 2, 1, 0.5$, and 0.05) at a scanning rate of 1 mV/s .

2.4.1. Governing equation

The voltammetric response of a two-electrode cell is governed by the principle of Kirchhoff's current law [1]. The law states that, a current that leaves from the positive electrode must equal the one that injects into the negative electrode. Therefore, we have

$$i^{\text{CELL}} = |i^{\text{P}}| = |i^{\text{N}}| \quad (7)$$

Eq. (7) plays a significant role as the governing equation throughout this work and it implies that the current response of a two-electrode cell must be determined by the minimum value of i^{P} and i^{N} . Regarding i^{P} and i^{N} , they can be easily obtained by applying Eq. (4) into Eq. (1) and Eq. (5) into Eq. (1a), respectively.

2.4.2. Initial condition

Before voltammetric scanning, the cell is kept at its as-assembled stage, namely at its initial condition. In this research, the two postulated electrodes are both pre-polarized fully to their unity x values ($x_{\text{O}} = 1$ and $x_{\text{R}} = 1$ for the positive and negative electrode, respectively) before cell assembling. This pre-treatment is a common pre-colouring step before putting a complementary ECD together. Meanwhile, a fixed charge capacity ratio is assigned to the cell. Hence, the initial condition for the cell's voltammetric simulation is written as follows

$$\begin{aligned} x_{\text{O}}^{\text{P}} = x_{\text{R}}^{\text{N}} = 1; \quad E^{\text{P}} = 2 \text{ V}, \quad E^{\text{N}} = -2 \text{ V}, \\ V^{\text{CELL}} = 4 \text{ V}; \quad i^{\text{CELL}} = i^{\text{P}} = i^{\text{N}} = 0 \quad (\text{at } t = 0) \end{aligned} \quad (8)$$

Briefly speaking, the cell is maintained at its fully charged state due to the fully pre-polarized step before voltammetric scanning.

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 (v) of 1 mV/s is applied to the simulated voltammetry for rationalizing the assumptions. Thus, we have

$$V^{\text{CELL}} = E^{\text{P}}(x_{\text{O}}^{\text{P}}) - E^{\text{N}}(x_{\text{R}}^{\text{N}}) = 4 - vt = 4 - 0.001t \quad (9)$$

and,

$$\frac{dV^{\text{CELL}}}{dt} = \frac{dE^{\text{P}}}{dt} - \frac{dE^{\text{N}}}{dt} = -v = -0.001 \quad (10)$$

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^{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, $i^{\text{CELL}}(t)$, $V^{\text{CELL}}(t)$, $E^{\text{P}}(t)$, and $E^{\text{N}}(t)$ are simulated for various charge capacity ratios from $t = 0 \text{ s}$ ($V^{\text{CELL}} = 4 \text{ V}$) to $t = 4000 \text{ s}$ ($V^{\text{CELL}} = 0 \text{ V}$).

3. Results and discussion

3.1. Parameters to determine the shape of a voltammogram

Simulated voltammograms (i^{CELL} versus V^{CELL}) of the cell for different charge capacity ratios ($R \equiv q^{\text{P}}/q^{\text{N}}$) 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. $x_i^j = 0$ ($i = \text{O}$ or R ; $j = \text{P}$ 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, $q^{\text{WO}_3} > q^{\text{PAni}}$, $q^{\text{WO}_3} < q^{\text{PAni}}$, and $q^{\text{WO}_3} = q^{\text{PAni}}$.

Fig. 5. The maximum discharge capacity of the cell, q^{CELL} ($\mu\text{C}/\text{cm}^2$), as a function of charge capacity ratio, which is obtained by integrating Fig. 4 against time.

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^{CELL} , 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, $9.65 \times 10^4 \mu\text{C}/\text{cm}^2$. As a consequence, the q^{CELL} – R relationship can be formulated by the following equation

$$q^{\text{CELL}} = \text{Min}(9.65 \times 10^4 \times R, 9.65 \times 10^4) \quad (11)$$

Since we have set $\Gamma_{\text{T}}^{\text{N}} = 10^{-6} \text{ mol}/\text{cm}^2$ and defined $R = q^{\text{P}}/q^{\text{N}}$, 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,

$$q^{\text{CELL}} = \text{Min}(q^{\text{P}}, q^{\text{N}}) \quad (12)$$

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 determine 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.)

Fig. 6. Digital simulation for the distribution of a cell's voltage on two electrodes for $R = 20, 2, 1, 0.5$, and 0.05 corresponding to Fig. 4.

In the case of $R = 1$, E^N and E^P are confined in their non-zero probability density function domains ($-2 \text{ V} \leq E^N \leq 0 \text{ V}$, $0 \text{ V} \leq E^P \leq 2 \text{ V}$) during the whole scanning period; that is, neither the positive electrode nor the negative one runs out (reaches at $x_j^i = 0$) before the final stage of the cathodic sweep. In the case when R -values are deviated from unity, we find that either the positive or negative electrode is exhausted before the end of scanning. As the electrode is exhausted, the cell's Faradaic process will be terminated, and the counter electrode's potential will be kept at a constant value.

These phenomena imply that the lower-capacity electrode in a cell is more prone to polarization than the larger-capacity one. Accordingly, when performing the two-electrode voltammetry for characterizing a working electrode, it would be better to maximize the charge capacity of the counter electrode, so that the counterelectrode can serve as a quasi-reference electrode more properly.

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 (ΔV^{CELL}) of a cell as the cell's voltage difference between the initial stage voltage (V_i^{CELL}) 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 ΔV^{CELL} and R , Eq. (9) is re-written in terms of q^j ($j = P$ or N) based on the principle of current continuity

$$V^{\text{CELL}} = E^P \left(x_O^P = \frac{q^P - q^{\text{Rxn}}}{q^P} \right) - E^N \left(x_R^N = \frac{q^N - q^{\text{Rxn}}}{q^N} \right) \quad (13)$$

where q^{Rxn} is the reacted charge capacity during the cathodic sweep. Because V_i^{CELL} (where $q^{\text{Rxn}} = 0$) has been given as 4 V for the fully pre-polarized electrodes, ΔV^{CELL} can be determined after calculating $V_{\text{cut}}^{\text{CELL}}$. In fact, $V_{\text{cut}}^{\text{CELL}}$ 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 $V_{\text{cut}}^{\text{CELL}} = E^P(0) - E^N(1 - R) = -E^N(1 - R)$

$$\text{for } q^P \leq q^N; R \leq 1 \quad (14)$$

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

$$\text{for } q^P \geq q^N; R \geq 1 \quad (15)$$

Based on the definition of ΔV^{CELL} , the relationship between ΔV^{CELL} and R is given correspondingly.

$$\begin{aligned} \Delta V^{\text{CELL}} &= [E^P(1) - E^N(1)] - [E^P(0) - E^N(1 - R)] \\ &= 4 + E^N(1 - R) \quad (R \leq 1) \end{aligned} \quad (16)$$

$$\begin{aligned} \Delta V^{\text{CELL}} &= [E^P(1) - E^N(1)] - [E^P(1 - R^{-1}) - E^N(0)] \\ &= 4 - E^P(1 - R^{-1}) \quad (R \geq 1) \end{aligned} \quad (17)$$

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.

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