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Determination of accurate electrode contribution during voltammetry scan of electrochemical capacitors

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Abstract

This paper introduces the method which allows determining the accurate electrode contributions during cyclic voltammetry (CV) scan of electrochemical capacitor. As a result of theoretical considerations, a calculation method which reveals voltammetry response of both electrodes during CV of two-electrode cell with reference is developed. The technique is based on the preservation of charge neutrality where the accurate potential sweep rate of individual electrode is dynamically assigned based on its total contribution to the total two-electrode cell voltage ramp. This practice should be used in the research with CV scans of energy storage devices in order to improve their precision. The technique is not an alternative to real three-electrode measurements, where constant sweep rate of working electrode is applied and an oversized auxiliary electrode is used, but it is rather a supplement, which allows observing the true electrode behavior during operation of the capacitor. The paper provides comparison of CV scans obtained with fixed scan rates of both electrodes with dynamic CV scan for electrochemical capacitors operating in aqueous media of 1 mol L^{-1} Li$_2$SO$_4$ and 7 mol L^{-1} KSCN. For the first time, the simple procedure is proposed to visualize the real qualitative electrode responses.

Introduction

Intensively developing area in electrochemical storage devices includes electrochemical capacitors (EDLC) [1]. Electrochemical capacitors are the devices, which are composed of separated electrodes impregnated with electrolyte containing ions as charge carriers [2, 3]. In order to achieve high double-layer capacitance values (Eq. (1)), the electrodes are made of porous material with developed surface area, e.g., activated carbon, which are connected to the external circuit via metallic current collectors [4].

$$C = \frac{\varepsilon A}{d} \qquad (1)$$

During ideal EDLC capacitor operation, the polarizable electrodes change their potential, meaning that the charges of opposite signs are attracted to the designated surfaces.

Upon charging, potential of positive electrode increases, while of the negative one decreases; thus, the potential difference (voltage) is created. In case when the electrode contains the species which are able to undergo redox reaction, the charge is consumed for the chemical potential change, and in turn, the counter electrode needs to balance the charge by accelerated increase of its electric potential. Finally, the cell voltage is governed by electrical double-layer (EDL) polarizable electrode, while the redox one is responsible for the increased cell capacitance as it can be found in hybrid capacitors [5–7]. In real capacitors utilizing electrode materials of high surface area, these two limiting conditions occur simultaneously and the final cell voltage is an outcome of partial chemical and electrical potential changes of the electrodes.

The measurements on electrochemical capacitors are very often carried out by voltammetry techniques in which the current response is recorded as a result of ramping voltage, dU/dt. It is clear that when both positive and negative electrodes change their electric potential by certain value, the absolute potential change of single electrode is not definable unless the third, non-polarizable electrode is used [8]. The voltammogram resulting from the scan of two-electrode electrochemical capacitor cell with reference electrode shows the response of both electrodes at the same time. It provides the information about charge exchange dynamics

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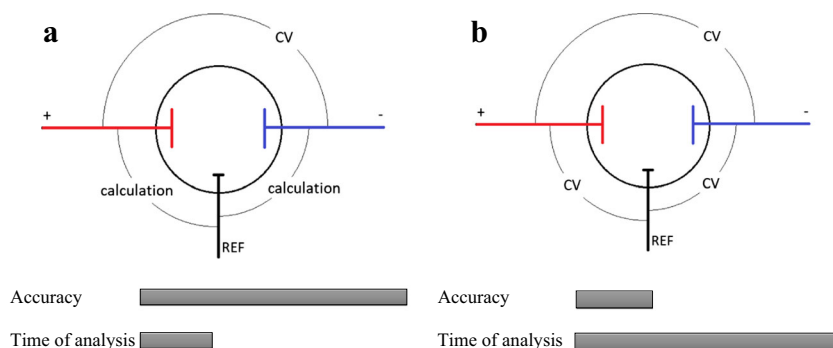   elzbieta.frackowiak@put.poznan.pl

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of full cell, which is the sum of two electrodes. The contribution and electrode kinetics of individual carbon electrode cannot be easily observed and separated during this two-electrode voltammetry experiment. Based on the shape of electrode potential increment during the sweep, one may only estimate whether the process ongoing at the electrode interface is faradaic or non-faradaic and define the working potential ranges of the electrodes, ΔE. However, up to date, no method revealing real potentiodynamic contribution of each electrode obtained during scan of two-electrode cell with reference electrode has been proposed. Hence, to overcome this limitation, a false approach is very often used. It is based on the scan of one polarizable carbon electrode versus reference electrode (treating second carbon electrode as an auxiliary one). Such experiments done for positive and negative electrode separately give an insight into the electrochemistry occurring at each side. Usually, these scans are conducted using fixed scan rates, dE/dt, obtained beforehand from the knowledge of total potential changes of electrodes ΔE^+ and ΔE^- from galvanostatic charge/discharge experiments. We aim to demonstrate here that the above approach is not always valid. The work presents a facile method to obtain real and true cyclic voltammetry curves of single electrodes obtained from only one measurement of the cell. Figure 1 presents the main features of method A, one measurement with reference electrode monitoring, and method B, which requires three independent measurements. Additionally, it has a tremendous effect on the time of analysis. It has never been proposed before.

The electrochemical capacitor can be modeled by two electrode/electrolyte interfaces representing both electrodes, i.e., two capacitors connected in series. Therefore the total voltage is equal to the sum of potentials changes of both electrodes (Eq. (2)).

$$U = \Delta E^+ + \Delta E^- \tag{2}$$

Differentiating both sides of Eq. (2), we obtain information that the total, strictly defined voltage scan rate is the sum of potential increments of each electrode (Eq. (3)).

$$\frac{dU}{dt} = \frac{dE^+}{dt} + \frac{dE^-}{dt} \tag{3}$$

In real EDLC, the capacitance is not constant and varies with potential applied; therefore, the scan rate attributable for single electrode is also not constant in time (Eq. (4)); hence, the previous methodology is false.

$$\frac{dE^+}{dt} = \frac{d\left(\frac{q^+}{C^+}\right)}{dt} \neq \text{const} \tag{4}$$

In order to link the total scan rate with electrode potential increment, the definition of the electrode scan rate for each increment time, dt, must be defined (Eq. (5)).
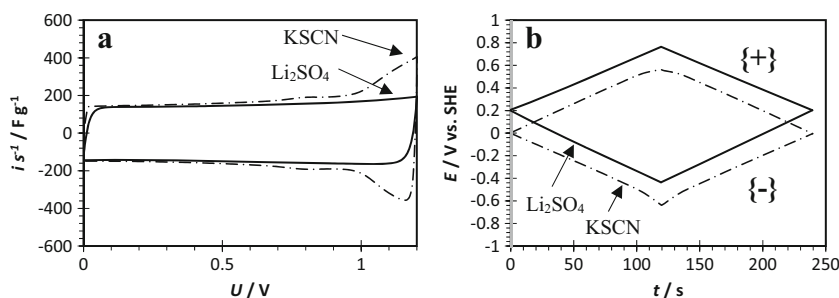
$$\frac{dU}{dt} = \frac{U_2 - U_1}{dt} \qquad \rightarrow \qquad dt = \frac{U_2 - U_1}{\frac{dU}{dt}} \tag{5}$$

The dt can now be inserted into the expressions for scan rates of single electrodes from Eq. (3) (Eq. (6)).

$$\frac{dE^+}{dt} = \frac{E_2^+ - E_1^+}{\frac{U_2 - U_1}{\frac{dU}{dt}}} \qquad \frac{dE^-}{dt} = \frac{E_2^- - E_1^-}{\frac{U_2 - U_1}{\frac{dU}{dt}}} \tag{6}$$

Now, the expression for scan rate of individual electrode can be calculated by inserting the difference between consecutive points of voltage and potential values recorded by the digital potentiostat for each infinite time increment through the entire voltammetry loop.

Fig. 1 Scheme representing the main features of the a method A and b method B. Method B requires three measurements, while method A requires only one in order to obtain three potentiodynamic curves

It is obvious that during the voltammetry scan, the same current flows through both electrodes which potentials change accordingly to the formulae in Eq. (6). Therefore, the capacitance at each point can be calculated using the measured current value and scan rate at each time increment, dt (Eq. (7)).
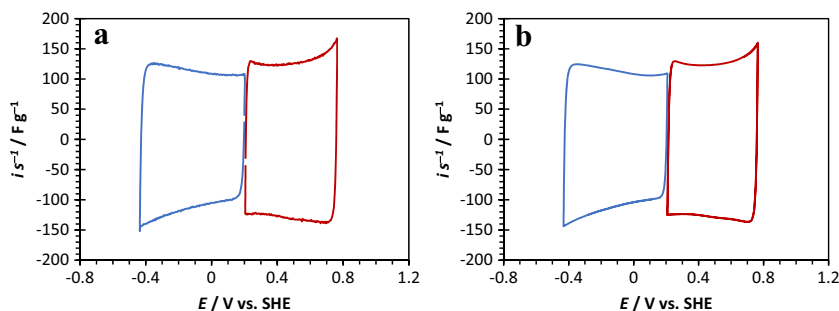
$$C^+ = \frac{I}{\frac{dE^+}{dt}} = \frac{I(U_2-U_1)}{\frac{dU}{dt}\left(E_2^+-E_1^+\right)} \tag{7}$$

The presented technique will allow obtaining the capacitance contributions of each electrode during voltammetry sweep of two polarizable electrodes cell (typical EDLC). It will exclude the necessity for separate measurements as often done in order to determine single electrode behavior [9, 10]. The comparison of the results obtained using above calculations (method A) and the method where both electrodes are investigated separately with fixed scan rate (method B) are shown and discussed in the paper.

Experimental

The electrodes for electrochemical capacitors are prepared from activated carbon Kuraray YP-80F (AC). The electrode composite comprises 97% of AC and 3% of polytetrafluoroethylene (PTFE) as the AC particle binder. Preparation of PTFE-bound electrodes is described in many studies [11]. The circular pellets of ca. 10 mg and 10 mm diameter disc electrodes are cut from the composite film.

Two cells are used in order to illustrate and compare both methods—one contains 1 mol L^{-1} Li$_2$SO$_4$ and the second 7 mol L^{-1} KSCN aqueous electrolytic solutions. Electrodes are separated by glass fiber separator Whatman GF/A and placed in two-electrode cell configuration (Swagelok) equipped with reference electrode (Hg/Hg$_2$SO$_4$ potential values recalculated further versus standard hydrogen electrode). Capacitor is investigated with cyclic voltammetry technique in the voltage range 0–1.2 V and full cell scan rate 10 mV s^{-1} (VMP3, Bio-Logic, France). The system contains electrodes of the same masses. All of the capacitance values, expressed as $i\,s^{-1}$, are normalized to the mass of one electrode active material. The electrode contributions according to method A are calculated based on the two-electrode scan with reference electrode. For method B, the scans of electrodes are done in three-electrode setup, separately for positive and negative one, with the scan rates determined during full cell scans, shown in the text.

Results and discussion

The two-electrode voltammetry scans with the sweep rate of 10 mV s^{-1} of systems operating in 1 mol L^{-1} Li$_2$SO$_4$ and 7 mol L^{-1} KSCN are shown in Fig. 2. Using neutral electrolyte essentially, electric double-layer response is observed within the electrochemical stability window of water. When the cell contains 7 mol L^{-1} KSCN, a significant redox contribution at high voltages is found together with EDL response, already thoroughly described [12].

Fig. 3 Electrochemical responses of negative and positive electrodes in 1 mol L^{-1} Li$_2$SO$_4$ polarized up to 1.2 V, according to method A (**a**) and method B (**b**)
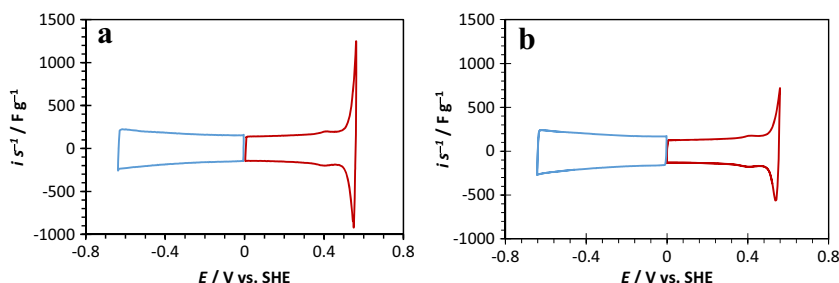
Fig. 4 Electrochemical responses of negative and positive electrodes in 7 mol L^{-1} KSCN polarized up to 1.2 V, according to method A (**a**) and method B (**b**)

The electrode potential profiles within the time of the experiment seem to be almost linear for Li_2SO_4. Considering their shape, they are probably without faradaic responses and contribute equally to the total voltage range. Therefore, the estimated scan rate attributable for one electrode is about half of total one, i.e., 5 mV s^{-1}. Contrarily, observing electrode potential profiles for the cell operating in KSCN, it is possible to see that the positive electrode is responsible for providing redox contribution, whereas the negative one has essentially EDL character. Based on the total potential ranges of each electrode, we may attribute 4.5 mV s^{-1} for positive electrode and 5.5 mV s^{-1} for negative electrode to ensure the same charge and discharge times. However, if a closer look is taken, it may be noticed that the electrode potential change (dE/dt) is not constant in time, what is especially seen close to the upper voltage limit of KSCN, where redox peak appears. It means that if one wants to observe the real behavior of electrodes during two-electrode cell operation, their scan rates should actually be variable to preserve the equal charge distribution on both electrodes. Figure 3 shows the electrode contributions of system operating in Li_2SO_4 obtained by method A which includes the variable scan rate and method B where the scan rate is fixed. In the capacitor in which redox contribution is not significant, the responses originating from both methods give almost identical characteristics.

On the other hand, the characteristics are different for the electrodes in the system with redox reactions (Fig. 4).

In that case, although the potential ranges of electrodes obtained via both methods are the same, their responses are significantly different (Fig. 4 a, b). First, it is seen that the current response of redox couple in Fig. 4b is lower than in Fig. 4a. Second, method A reveals clearly defined reduction peak occurring at positive electrode. This difference originates from the fact of unequal charge distribution and the fact that the electrochemical signature in method A is driven by the current, while in method B, by the potential. When the cell voltage rises (Fig. 4a), the gradual increase of positive electrode capacitance is automatically balanced by accelerating potential scan rate of negative electrode. It aims to satisfy the condition of equilibrium presented in Eq. (8) all the time. It means, integer of charging/discharging curves of positive and negative electrode are identical.

$$q^+ = q^-$$
$$C^+ \cdot \Delta E^+ = C^- \cdot \Delta E^- \qquad (8)$$

In case when the scan rates for electrodes are fixed and determined beforehand (as in method B), this condition is not satisfied and become more inaccurate when the respective electrode capacitances are variable.

Method B is a typical three-electrode measurement, where the potential of only one electrode (working) is controlled while the second one (auxiliary) is neglected. According to the results and theoretical considerations, method A can be treated as a technique to reflect the real and accurate potentiodynamic curves assignable for both individual electrodes during operation of two-electrode electrochemical cell. In some cases, where respective electrode capacitances are the same, the methods presented give similar result (Fig. 3) but the care with their interpretation should be kept. In case when the electrode capacitances are variable, method A can be successfully used for monitoring of electrodes behavior, while method B is no longer valid.

Conclusions

The paper presents a method for extraction of the accurate potentiodynamic contribution of two polarizable electrodes (two-electrode system) in electrochemical capacitor when reference electrode is attached. The potentiodynamic curves reveal the real and charge-balanced behavior of the electrodes during single CV experiment. It excludes the measurements of both electrodes separately which significantly reduces the time of investigation while ensuring perfect accuracy. The integration of electrode voltammograms exactly reflects the two-electrode response of the electrochemical capacitor. The advantage of method A is that it can help scientists in describing the online behavior of electrodes in accurate and quick way. Surely, it is especially useful in the area of electrochemical energy storage devices. The method can contribute to the more reliable electrochemical characterization of the devices, as the electrode responses are obtained simultaneously in dynamic way. The dynamic method A does not require separate

measurements for single electrodes. Therefore, the risk of errors associated with wire manipulations and unexpected potential fluctuations during the investigation is eliminated. The method B, which uses constant scan rate, gives artificial view of electrodes, which does not actually take place during two-electrode capacitor cell operation.

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