



Effects of charge redistribution on self-discharge of electrochemical capacitors

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ABSTRACT

The effect of charge redistribution on the self-discharge profile of porous carbon (Spectracarb 2225) electrodes is examined. A model pore based on the de Levie transmission line circuit is used to show that self-discharge due purely to charge redistribution results in the same self-discharge profile as that expected for an activation-controlled self-discharge mechanism (the potential falls linearly with $\log t$), thus the linear log time profile is not characteristic of an activation-controlled mechanism. The addition of a hold step reduces the amount of charge redistribution in porous carbon electrodes, although the hold time required to minimize the charge redistribution is much longer than expected, with electrodes which have undergone a 50 h hold time still evidencing charge redistribution effects. The time required for the charge redistribution through the porous electrode is also much greater than predicted, likely requiring tens of hours. This highlights the importance of the charge redistribution in self-discharge of systems using porous electrodes, such as electrochemical capacitors.

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1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors, and ultracapacitors are charge storage devices. They may store charge in a Faradaic reaction as pseudocapacitance or may store charge in the double-layer of an electrode/electrolyte interphase [1]. Double-layer ECs typically utilize high surface area electrodes (often, carbon which may have a Brunauer, Emmett and Teller (BET) surface area of up to 2500 m²/g). The high surface area is necessary since the charge is stored in the electrode/electrolyte boundary region, and a higher surface area results in more charge storage. By necessity, this requires very small pores in the electrodes, and these small, often very tortuous pores, lead to significant diffusion and migration limitations down the pores during charging/discharging [3]. A mathematical evaluation of the potential and current distribution in porous electrodes was previously given by de Levie [3], which showed that the electrode processes do not proceed evenly throughout the thickness of a porous electrode, largely due to the IR drop in the solution within the pores, resulting in faster electrode processes at the mouth of the pore, closer to the counter electrode, versus those which occur at the base of the pore [2]. In other words, the external surface of the electrode will charge/discharge faster than the surfaces within the pores. This behavior can be modeled with an RC transmission line [2]. As a result of this pore effect and its transmission line characteristics, when a porous electrode is charged there will be a distribution of potentials down the electrode

pores. As the system is switched to open-circuit these potentials will equilibrate as the charge redistributes evenly over the electrode surface [4]. The potential at the tip of the pore, where the potential is measured, will fall during this charge redistribution, and may appear as a rapid, initial self-discharge.

Self-discharge is the spontaneous decline in voltage with time of a charged EC left on open-circuit. The rate of self-discharge is determined by the mechanisms of the processes by which the self-discharge takes place [5]. When a charged EC is placed on open-circuit there is no external circuit through which electrons may pass and discharge the cell, and therefore self-discharge must take place through coupled anodic and cathodic processes. Conway et al. [5] proposed three mechanisms through which self-discharge may occur, and derived models which describe the predicted self-discharge profile for each mechanism:

- (i) An activation-controlled Faradaic process, where the decline of voltage (V or V_t) versus log time would give a straight line [5,6]:

$$V = -\frac{RT}{\alpha F} \ln \frac{\alpha F i_0}{RT C} - \frac{RT}{\alpha F} \ln \left(t + \frac{C\tau}{i_0} \right) \quad (1)$$

and

$$V_t = V_i - A \log(t + \tau) \quad (2)$$

where R is the universal gas constant, T is the absolute temperature, α is the charge transfer coefficient, F is the Faraday constant, i_0 is the exchange current density, C is the capacitance, t is the time, τ is an integration constant, V_i is the initial charging potential and A is a constant related to the Tafel slope. This model describes the self-

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discharge due to the Faradaic reaction of a species which is either at high concentration in the cell (e.g. electrolyte decomposition [7]) or is attached to the surface (e.g. oxidation/reduction of a carbon surface functionality [8]).

(ii) A diffusion controlled Faradaic process where the potential would decline with the square root of t [6]:

$$V_t = V_i - \frac{2zFAD^{1/2}\pi^{1/2}c_0}{C} t^{1/2} \quad (3)$$

where D is the diffusion coefficient of the redox species, z is the charge, c_0 is the initial concentration and A is the electroactive area. This model is based on the Faradaic reaction of a species which has a low concentration in the EC and relies on transport (diffusion) to the electrode surface to react (e.g. an Fe shuttle reaction [6]).

(iii) An internal ohmic leakage or a 'short circuit' due to faulty construction. Here a plot of $\ln V_t$ versus t would give a linear relationship [6]:

$$\ln V_t = \ln V_i - \frac{t}{RC} \quad (4)$$

where R is the resistance of the ohmic contact.

It was previously shown by Niu et al. [6] that the self-discharge profile of a highly porous Spectracarb 2225 carbon cloth was linear when voltage was plotted versus $\log t$, suggesting that the self-discharge proceeded through an activation-controlled Faradaic mechanism. It was also shown in Ref. [6] that the slope of the self-discharge profile when plotted as a function of $\log t$ was dependent upon the initial potential of the electrode, contrary to that predicted by Eq. (2). Niu et al. [6] suggested that the slope dependence on the initial potential may be due to a charge redistribution effect in the porous electrode, as the amount of charge redistribution experienced will be dependent on the polarization potential. In this work the effect of charge redistribution on self-discharge was elucidated, including an examination of the self-discharge which results purely from charge redistribution and a discussion of the time domains required for this charge redistribution to complete in highly porous electrodes.

2. Experimental

2.1. Electrodes, cell and procedure to reach steady-state

Each working electrode was composed of a ca. 10 mg piece of Spectracarb 2225 carbon cloth (Spectracorp, BET surface area = 2500 m²/g) mounted in a Teflon Swagelok system (PFA tube fitting) with ionically insulating, electronically conducting current collectors (supplied by Axion Power International Inc.), and electrical contact to a Pt wire, sealed in glass tubing. Counter electrodes were fabricated from the same carbon cloth, wrapped with Au wire for electrical contact. A standard hydrogen electrode (SHE) was used as a reference electrode, and all potentials in this paper are referenced to it.

Experiments were performed in a three-compartment, three-electrode glass cell filled with 1.0 M H₂SO₄ prepared from concentrated H₂SO₄ (Sigma-Aldrich, 99.999% pure) and 18 MΩ water. The reference compartment was separated from the working electrode compartment via a luggin capillary. Nitrogen was bubbled through the working and counter electrode compartments prior to and during experiments to remove O₂ from the electrolyte. The experiments were conducted at 22 ± 3 °C. All measurements were performed using a Princeton Applied Research VMP3 multipotentiostat. Data was collected using EC-Lab software.

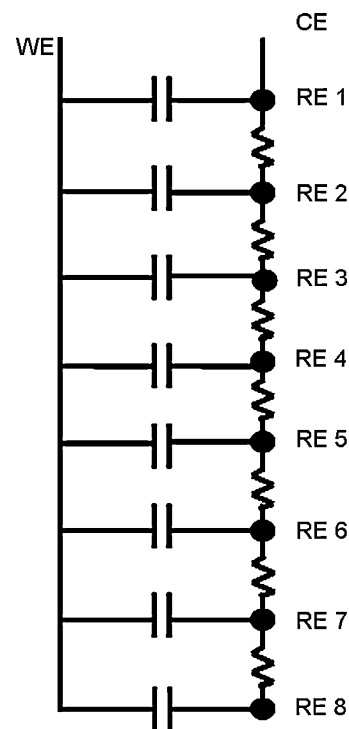


Fig. 1. Schematic of the hardware transmission line circuit, based on de Levie's [3] transmission line model of a pore.

Working electrodes were cycled between 0.0 and 1.0 V versus SHE using a sweep rate of 1 mV/s for approximately 1 week (~300 cycles) prior to self-discharge measurements in order to bring the electrodes to a steady-state whereupon no further changes in the shape or size of the cyclic voltammograms were seen. The 0.0 and 1.0 V potential limits were used since at potentials outside of these limits undesirable, irreversible Faradaic reactions occur which destroy the carbon cloth electrode.

2.2. Transmission line circuit

A hardware transmission line circuit was used as a model pore, based on the de Levie [3] transmission line model. A schematic of the hardware transmission line circuit used in this work is shown in Fig. 1. It consists of eight parallel sections, with each section being composed of a resistor and capacitor in series. The resistors model the solution resistance down the pore which leads to the potential drop down the pore during charging/discharging (based on Ohm's law). The capacitors model the capacitance of the double-layer at the electrode/electrolyte interface. The value of the resistance can be set to a value between 10 and 100 kΩ in 10 kΩ increments or to 200 or 300 kΩ. Each capacitor was made up of a parallel combination of ten 10 μF/6.3 V multilayer ceramic chip capacitors, for a nominal capacitance of 100 μF. The capacitors in the hardware circuit could be shorted out and were brought to a zero charge state (0 V) prior to each experiment.

A VMP3 multipotentiostat was used to track the potentials at each terminal (RE 1–8) by connecting the working electrode (WE) leads of the multipotentiostat together with connection to the WE point on the hardware circuit (as shown by WE in the schematic in Fig. 1). Similarly, the counter electrode (CE) lead of terminal 1 was connected to the CE point. The reference electrode (RE) leads of each of eight channels were connected to points RE 1–8 of the hardware circuit.

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