



# Determination of the upper and lower potential limits of the activated carbon/propylene carbonate system for electrical double-layer capacitors



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## ABSTRACT

This study demonstrates the criteria for determining the working potential window of commercial activated carbons (ACs) in the propylene carbonate-based (TEABF<sub>4</sub>/PC) electrolyte for electrical double-layer capacitors (EDLCs). Through a common potential-floating examination, the working potential window of ACs in 1 M TEABF<sub>4</sub>/PC is between  $-2.0$  and  $0.3$  V (vs. Ag/AgNO<sub>3</sub>). However, an EDLC consisting of the above ACs in 1 M TEABF<sub>4</sub>/PC with charge/discharge in this potential window for 1152 cycles shows 27% capacitance loss. The electrochemical impedance spectroscopic (EIS) analyses show the presence of an obvious impedance arc behind the high-frequency semicircle on both positive and negative electrodes after the charge–discharge (CD) cycling. Consequently, a combination of a potential-floating test and EIS analyses precisely determines the working potential window between  $-1.9$  and  $0.2$  V, which is a reliable method to efficiently define the working potential window. In this potential range, an EDLC exhibits about 6% capacitance loss during the CD test for 10,000 cycles. The EIS results also reveal an acceptable capacitor behavior after the 10,000-cycle CD test.

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## 1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors, generally exhibit superior capabilities in high-rate electricity charge/discharge and cycle life [1]. The above characteristics of ECs have been demonstrated to promote the energy capture efficiency of regenerative energy sources as well as energy storage systems and to create new functions when both devices are integrated. Based on the charge storage mechanism, ECs can be divided into three categories: (1) electrical double-layer capacitors (EDLCs), (2) redox pseudocapacitors, and (3) asymmetric supercapacitors (ASCs).

For improving the energy density of ECs, how to enlarge the cell voltage is one of the most efficient strategy [2]. The most effective way to extend the cell voltage is utilization of organic electrolytes or ion liquids. For example, Andrea Balducci et al. [3] developed innovative solvents and salts for extending the cell voltage from 2.5–2.7 V to 3.2 V, clearly demonstrating this idea. On the other hand, how to precisely determine the working potential window is an important issue since the interface properties of any system are strongly affected by both electrode materials and electrolytes. For instance, AC-based EDLCs with commercial organic electrolytes such as acetonitrile- and propylene carbonate-based (AN & PC) electrolytes show a cell voltage of 2.5–2.7 V [4,5]. However,

an irreversible oxidation on AC in PC electrolytes at 0.1 V vs. Ag/AgNO<sub>3</sub> has been found [6], probably due to interactions among organic electrolyte, residual water, and oxygen-containing functional groups of AC. When EDLCs were operated at relatively high cell voltages (e.g.,  $>2.7$  V), the capacitance decay accompanies the gaseous products of CO<sub>2</sub> and CO on the positive electrode side and CO<sub>2</sub>, CO, H<sub>2</sub>, ethylene and propylene on the negative electrode side, respectively [7,8]. The gaseous products on the positive electrode side are mainly due to the reaction(s) between oxygen-containing functional groups on the surface of AC and electrolyte during the solid electrolyte interface (SEI) formation, while the residual water reduction and electrolyte decomposition occur on the negative electrode side simultaneously [9, 10]. The above gaseous products raise the pressure of devices [11] and reduce the electrode cohesion [8]. Besides the gaseous products, the SEI film was formed at cell voltages  $>3.5$  V, leading to a higher resistance on the electrode [8,12]. Consequently, the capacitance significantly decays and the equivalent series resistance (ESR) markedly increases [5,13].

Nowadays, numerous methods have been developed for testing the extremely high cycle life of ECs in order to gain a reliable energy storage device [14,15]. Recently, the potential-stressed floating tests attract much attention for determining the maximal working potential window of ECs [16]. Such tests are generally conducted at specified potential biases/cell voltages for a period in order to gain the quasi-steady-state current density ( $i_{SS}$ ). From the plot of  $\log(i_{SS})$  against electrode potential/cell voltage, a significant increase in  $i_{SS}$  between two potential biases or cell voltages indicates the occurrence of Faradaic reactions at

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the more stressed potential or cell voltage [13,17]. On the other hand, electrochemical impedance spectroscopy (EIS) has also been proposed to be a powerful tool for examining the maximal cell voltage [14] and degradation mechanisms of energy storage devices [15,16]. Hence, the combination of EIS analysis and the potential-stressed floating test is complementary, which is proposed here to be a precise method for determining the working potential window of ACs in organic electrolytes. The key challenge of this work is to correlate the results of potential-stressed floating and charge–discharge (CD) cycling tests to the EIS data. Therefore, the combined technique proposed in this work is both of practical and academic interests because this technique not only clarifies the routes of capacitance decay of a full cell but also identifies the possible degradation/variations on the positive and negative electrodes, separately.

## 2. Experimental

### 2.1. Electrode preparation

A commercially available activated carbon (denoted as AC; ACS-679, China Steel Chemical Corporation, Taiwan; specific surface area:  $1635 \text{ m}^2 \text{ g}^{-1}$ ) was uniformly mixed with polyvinylidene difluoride (PVDF, 10 wt.%) and *N*-methyl-pyrrolidinone for 30 min. The coating slurry was drop-casted onto a pre-treated graphite electrode with an exposed geometric surface area of  $1 \text{ cm}^2$  to form the working electrode under the three-electrode mode. The procedure of graphite pre-treatments completely followed our previous work [18]. A platinum helix and an Ag/AgNO<sub>3</sub> electrode (Argenthal, 0.01 M AgNO<sub>3</sub>, 0.1 M tetrabutylammonium perchlorate dissolved in AN) were used as the counter and reference electrodes, respectively. The standard electrolyte used for the electrochemical tests was a propylene carbonate (PC) solution containing 1 M tetraethylammonium tetrafluoro-borate (TEABF<sub>4</sub>) in a beaker cell. For the two-electrode mode, the symmetric cell consisted of two AC-coated electrodes without a separator. The position of the above two electrodes was fixed to maintain a constant distance (5 mm).

### 2.2. Characterization

The electrochemical characteristics of ACs were examined by an electrochemical analyzer system, CHI 760E (CH instruments, USA), under three-electrode or two-electrode modes using chronoamperometry (CA, *i*-*t* curve), chronopotentiometry (CP, *E*-*t* curve), and electrochemical impedance spectroscopy (EIS). The alternating-current potential amplitude in the EIS measurement was equal to 5 mV with its frequency range between 100 kHz and 0.01 Hz. All the above electrochemical tests were conducted in a nitrogen-filled glove box (MBRAUN, Germany) containing < 1 ppm H<sub>2</sub>O and O<sub>2</sub>. The X-ray photoelectron spectroscopic (XPS) measurements were

performed on a PHI Quantera SXM (ULVACPHI, Japan) which employed the Al monochromator irradiation as the photosource.

## 3. Results and discussion

### 3.1. Determining the working potential window from the potential-stressed floating test

In this work, the potential-stressed floating test is defined as the process where the electrode containing ACs are polarized at specified potentials under the three-electrode mode for 3000 s to obtain the quasi-steady-state current density ( $i_{SS}$ ). If any irreversible oxidation or reduction occurs at the electrolyte/AC at the specified potential,  $i_{SS}$  will significantly rise. Hence, a plot of  $\log(i_{SS})$  vs. electrode potential (see Fig. 1a and b) is obtained to determine the upper or lower limits of the working potential window if an obvious increase in  $\log(i_{SS})$  is found.

Fig. 1a is employed to determine the upper limit of the working potential window by varying the electrode potentials from 0 to 0.6 V. Clearly, two linear regions were found for  $\log(i_{SS})$  vs. electrode potential and only ca. 6% increase in  $\log(i_{SS})$  is found when the electrode potential is gradually shifted from 0 to 0.3 V. Then, there is a more obvious increase in  $\log(i_{SS})$  to 13% when the electrode potential is further positively shifted from 0.3 to 0.4 V. This phenomenon is considered the occurrence of a significant irreversible oxidation at the AC/electrolyte interface because of the relatively high activity of oxygen-containing functional groups [8]. Accordingly, 0.3 V is regarded as the upper limit of the working potential window.

Fig. 1b is employed to identify the lower limit of the working potential window by negatively shifting the electrode potential from the rest potential of AC in the PC electrolyte (denoted as  $E_{rest}$ , ca.  $-0.6 \text{ V}$ ) to  $-2.2 \text{ V}$ . The  $\log(i_{SS})$  between  $-0.6$  and  $-2.1 \text{ V}$  shows very similar quasi-steady-state current densities. However,  $\log(i_{SS})$  markedly increases when the electrode potential is shifted from  $-2.1$  to  $-2.2 \text{ V}$ , attributable to the significant occurrence of an irreversible reduction at  $-2.2 \text{ V}$ . Hence,  $-2.1 \text{ V}$  is regarded as the lower limit of the working potential window. According to the above results and discussion, the working potential window of ACs in the TEABF<sub>4</sub>/PC electrolyte is limited from 0.3 V to  $-2.1 \text{ V}$ .

In order to confirm the above working potential window, two AC electrodes were assembled into a two-electrode cell containing 1 M TEABF<sub>4</sub>/PC solution, and tested with a cell voltage of 2.3 V. The mass loading on positive and negative electrodes were adjusted according to the charge balance consideration [19]. This cell was initially charged and discharged at  $0.5 \text{ A g}^{-1}$ , which exhibits a slightly asymmetric charge–discharge (CD) curve between 2.1 and 2.3 V (see curve (1) in Fig. 2a). This phenomenon suggests voltage stress (polarization) on the cell when the cell voltage is between 2.1 and 2.3 V. Note that the total time for 1 CD cycle between 2.1 V and 2.3 V at  $0.5 \text{ A g}^{-1}$  is 28.1 s. Hence, the application of 128 CD cycles is very similar to the voltage-

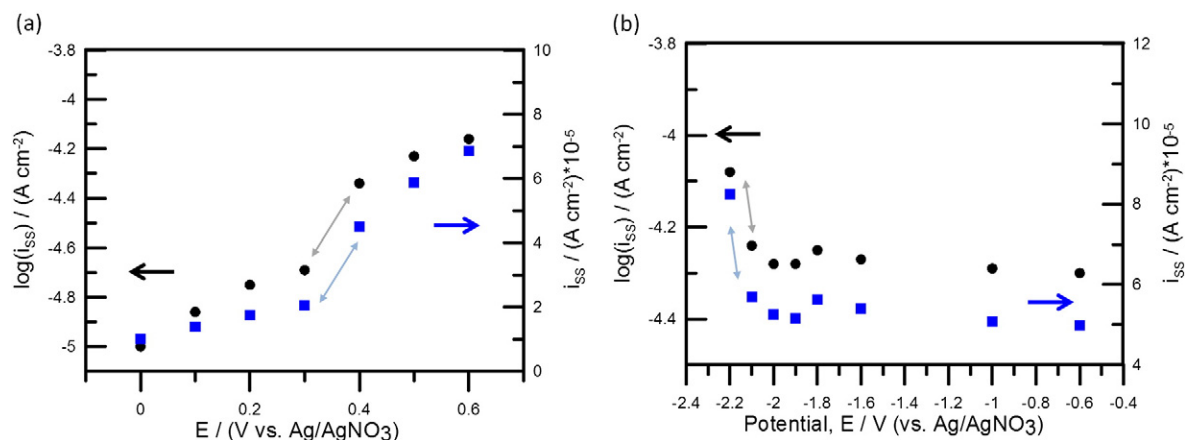


Fig. 1.  $\log(i_{SS})$  and  $i_{SS}$  from the floating test for 3000 s at potentials located (a) between 0 and 0.6 V and (b) between  $E_{OCP}$  ( $-0.6 \text{ V}$ ) and  $-2.2 \text{ V}$  vs. Ag/AgNO<sub>3</sub>.

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