



The influence of current collector corrosion on the performance of electrochemical capacitors



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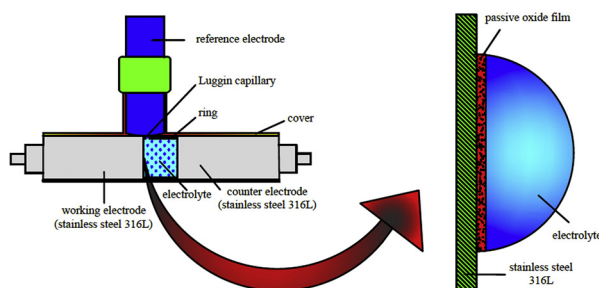
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HIGHLIGHTS

- Corrosion potential of stainless steel is lowest in alkaline solutions.
- Different forms of passive oxide film are formed on the surface of stainless steel.
- Supercapacitor parameters are deteriorated by the corrosion of current collectors.
- High-voltage supercapacitor is a result of presence of stable passive oxide film.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper discusses the effect of current collector (stainless steel 316L) corrosion on the performance of electrochemical capacitors operated in aqueous electrolytes. This topic seems to be often neglected in scientific research. The studied electrolytes were 1 M H₂SO₄, 1 M KI, 1 M Na₂SO₄, 1 M KOH and 6 M KOH. The corrosion process was investigated by means of selected direct and alternating current techniques. The surface of the current collectors as well as the corrosion products were characterised using scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy and atomic force microscopy. Stainless steel 316L in alkaline solutions is characterised by the lowest values of corrosion potentials whereas the potentials in acidic media become the most noble. Our studies show that corrosion potentials increase with decreasing pH value. This phenomenon can be explained with the formation of passive oxide films on the stainless steel current collectors. The passive oxide films are usually thicker and more porous in alkaline solutions than that in the other electrolytes. The processes occurring at the electrode/electrolyte interfaces strongly influence the working parameters of electrochemical capacitors such as voltage, working potentials of single electrodes, self-discharge as well as the internal resistance and cycling stability.

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1. Introduction

There is an increasing research and development on electrochemical capacitors (ECs) that can be used for energy storage. Electrochemical capacitors are able to store electrical charge in the electric double layer or via additional Faradaic reactions (so-called

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pseudocapacitive effect). Electrochemical capacitors consist of two separated electrodes immersed in an electrolyte. The most commonly used electrode materials for such systems are carbon materials such as activated carbon, carbon nanotubes, carbon aerogels and graphene [1–4].

Batteries and fuel cells are high energy devices, while dielectric capacitors are characterized by high specific power. Therefore, electrochemical capacitors bridge the gap between aforementioned devices and could be used to improve their performance. It should be noted that improving the energy density of ECs is still a technological and scientific challenge. The energy E is proportional to the capacitance C , and the square of the voltage U according to equation (1) [5,6]:

$$E = \frac{1}{2} CU^2 \quad (1)$$

The voltage of electrochemical capacitors is limited by the stability of the electrolytes. In the case of aqueous electrolytes the operating voltage is usually less than 1 V. On the other hand organic electrolytes or ionic liquids allow extending the voltage beyond 2 V [7]. Unfortunately, organic electrolytes are characterised by higher resistances compared to aqueous systems. Moreover, aqueous electrolytes are less expensive than organic electrolytes and do not require purification and drying processes. It should be noted that exceeding the operating voltage could damage the whole system due to the internal overpressure. It is worth mentioning that electrochemical capacitors working in sodium sulfate electrolyte can reach 1.6 V or even 2 V in the case of lithium sulfate [6,8].

Apart from the low specific energy, one of the main drawbacks of electrochemical capacitors is self-discharge. Self-discharge is the spontaneous loss in voltage with time at open circuit conditions. Three main mechanisms for self-discharge are discussed in literature: activation-controlled Faradaic processes, diffusion controlled Faradaic processes and internal ohmic leakage. Taking into account these processes, understanding the phenomena occurring at the electrode/electrolyte interface is essential for optimizing the working parameters of electrochemical capacitors. Therefore, during such investigations the behaviour of not only the active electrode materials, electrolyte but also current collectors should be taken into consideration [9,10].

In power sources, current collectors are usually composed of copper, aluminium or stainless steel. It should be noted that during cycling the current collectors may suffer some corrosion. The corrosion processes can take place on the positive and negative electrode. The polarisation process may result in dissolution of the current collector surface, ion intercalation, etching as well as passivation [11,12]. Besides electrochemical capacitors, many scientists focused on corrosion phenomena occurring on the current collectors utilized in batteries e.g. in lithium-sulfur cells [13–15]. In this type of devices there is formation of lithium polysulfides and insulating lithium sulfide compounds which are responsible for the deterioration of the operating parameters. Ryu et al. [13] found that formation of those compounds is an effect of corrosion phenomena occurring at the current collectors of 316 type stainless steel. Zhang et al. [14] demonstrated the influence the electrolyte composition of lithium-sulfur cells on the aluminium current collector corrosion.

This paper discusses the behaviour of current collectors in electrochemical capacitors operated in aqueous solutions, a topic which to the best of our knowledge is often neglected in scientific research and has not been extensively studied in terms of corrosion processes. The objective of this work is to determine the factors determining the performance of carbon/carbon supercapacitors with stainless steel current collectors. The corrosive properties and

capacitive characteristics of ECs were determined by means of selected electrochemical methods. Moreover, the surface morphology and physicochemical properties of the current collectors were characterized.

2. Experimental

2.1. Electrochemical measurements

Electrochemical measurements were performed in three-electrode Swagelok[®] cells with five different electrolytes and corresponding reference electrodes (Table 1). At the beginning, the current collectors (ITALINOX Poland Ltd.), made of stainless steel 316L (composition: ≤ 0.03 wt-% C, ≤ 1.0 wt-% Si, ≤ 2.0 wt-% Mn, max 0.045 wt-% P, ≤ 0.015 wt-% S, ≤ 0.11 wt-% N, 16.5–18.5 wt-% Cr, 2.0–2.5 wt-% Mo, 10.0–13.0 wt-% Ni) were cleaned mechanically with abrasive paper 2500 and degreased in a solution containing 15 g dm⁻³ NaOH and 30 g dm⁻³ Na₃PO₄ × H₂O (298 K, 10 min). Afterwards, the samples were etched in 1 M HCl (298 K, 5 min). Between each step, the samples were cleaned with distilled water in an ultrasonic bath for 15 min. In order to perform electrochemical measurements, the Swagelok[®] system was assembled with suitable reference electrode and two stainless steel 316L current collectors, separated by a ring with diameter of 12 mm and height of 10 mm. One of those collectors served as a working electrode, while the other was used as a counter electrode. In order to maintain ionic conductivity between working and reference electrode, a small hole was drilled on the top of the ring at a distance of 1 mm from the working electrode. The space in the center of the ring was filled with one of the electrolytes presented in Table 1. The hole performed the function of a Luggin capillary. The above Swagelok[®] system is presented in Fig. 1(a).

First, the open circuit potential (OCP) was measured for 180 min. Then, linear polarisation (LP) tests were carried out at 0.2 mV s⁻¹. The working electrode was polarised cathodically to -250 mV vs OCP and then anodically to 250 mV vs OCP.

In the next part of the study, the Swagelok[®] system with fresh electrolyte and current collectors was assembled. After the OCP measurements, electrochemical impedance spectroscopy (EIS) tests were performed in the frequency range 100 kHz to 10 mHz. The amplitude was ± 10 mV with respect to the OCP. After that, cyclic potentiodynamic polarisation (CPP) studies were carried out. The electrode was first polarised cathodically to -100 mV vs OCP, then anodically, until current values of 100 μ A were reached. The scan rate was 0.2 mV s⁻¹.

Commercial steam activated carbon (AC) (Norit[®] GSX, Alfa Aesar) was used as the electrode material of an electrochemical capacitor. The electrode was composed of 85 wt% activated carbon, 10 wt% polyvinylidene fluoride (Kynar Flex 2801) as a binder and 5 wt% acetylene black. The electrochemical tests were carried out by using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The electrochemical measurements were carried out with two- and three-electrode

Table 1
Electrolytes and reference electrodes used in electrochemical measurements.

Electrolyte	pH	Reference electrode	Potential vs NHE (V)
1 M H ₂ SO ₄	0.0	Hg/Hg ₂ SO ₄ in 1 M H ₂ SO ₄	0.674
1 M Na ₂ SO ₄	5.4	Hg/Hg ₂ SO ₄ in 0.5 M K ₂ SO ₄	0.640
1 M KI	6.6	Hg/Hg ₂ Cl ₂ in saturated KCl	0.244
1 M KOH	14.9	Hg/HgO in 6 M KOH	0.085
6 M KOH	15.9	Hg/HgO in 6 M KOH	0.085

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