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Chemical etching of stainless steel 301 for improving performance of electrochemical capacitors in aqueous electrolyte

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HIGHLIGHTS

- We have chemically pitted stainless steel foil to enhance surface roughness.
- AFM and SEM reveal uniform pitting, with diameter of pits ranging from 100 to 300 nm.
- We have realized EDLCs with coated electrodes prepared from the pitted foil.
- Excellent coating adhesion dramatically reduces equivalent distributed resistance.
- The EDLCs display good charge propagation and ability to operate at high power.

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ABSTRACT

The main purpose of the study was to increase the surface roughness of stainless steel 301 current collectors by etching, in order to improve the electrochemical performance of electrical double-layer capacitors (EDLC) in 1 mol L^{-1} lithium sulphate electrolyte. Etching was realized in 1:3:30 (HNO_3:HCl:H_2O) solution with times varying up to 10 min. For the considered 15 μm thick foil and a mass loss around 0.4 wt.%, pitting was uniform, with diameter of pits ranging from 100 to 300 nm. Atomic force microscopy (AFM) showed an increase of average surface roughness (Ra) from 5 nm for the as-received stainless steel foil to 24 nm for the pitted material. Electrochemical impedance spectroscopy realized on EDLCs with coated electrodes either on as-received or pitted foil in 1 mol L^{-1} Li_2SO_4 gave equivalent distributed resistance (EDR) of 8 Ω and 2 Ω, respectively, demonstrating a substantial improvement of collector/electrode interface after pitting. Correlatively, the EDLCs with pitted collector displayed a better charge propagation and low ohmic losses even at relatively high current of 20 A g^{-1}. Hence, chemical pitting of stainless steel current collectors is an appropriate method for optimising the performance of EDLCs in neutral aqueous electrolyte.

1. Introduction

Electrochemical capacitors, also called supercapacitors, are very promising energy storage devices, applied both in stationary and mobile systems for delivering high power pulses [1–3]. Since the energy density of supercapacitors is proportional to the square of voltage, most of the devices available in the market are based on organic electrolytes, e.g., tetraethylammonium tetrafluoroborate in acetonitrile or propylene carbonate, despite their harmfulness, toxicity, flammability and moderate conductivity. Because of these disadvantages, many investigations have been lately conducted in order to replace the organic electrolytes by less harmful and hazardous electrolytes such as ionic liquids and aqueous solutions. The main advantages of aqueous electrolytes are their high conductivity, environmental friendliness and low cost of the capacitor systems which can be assembled in ambient conditions [3]. However, capacitors based on the most popular aqueous solutions, i.e. H_2SO_4 and KOH, are not able to operate at voltages higher than 0.7–0.8 V [4]. Lately, it has been demonstrated that voltages up to 1.6–2.0 V can be reached by using aqueous solutions of alkali sulphates and gold current collectors [5,6]. Potentiostatic floating on supercapacitors made of stainless steel current collectors and activated

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carbon (AC) electrodes in 1 mol L^{-1} Li_2SO_4 electrolyte proved that these systems are able to withstand 1.5 V at room temperature without noticeable corrosion of the collectors [7,8]. Hence, it makes sense to plan optimizing such capacitors for further developments.

Usually, electrodes of industrial capacitors in organic electrolyte are made by coating aluminium current collector with a slurry constituted of activated carbon, conductive additive (carbon black) and a binder (either polyvinylidene fluoride – PVdF – dissolved in N-methyl-2-pyrollidone, or polytetrafluoroethylene – PTFE – in water suspension). It has been previously shown that the adhesion of the coating layer can be enhanced by etching the aluminium surface either chemically with 1 mol L^{-1} HCl at 80 °C for 2 min [9] or by anodic oxidation of aluminium foil immersed in 1 mol L^{-1} HCl at 80 °C using a current of 200 mA cm^{-2} for 20 s [10]. Therefore, the objective of this paper is to determine the etching conditions of stainless steel in order to improve the performance of AC/AC supercapacitor cells in 1 mol L^{-1} Li_2SO_4, by using coated collectors based on the etched material.

Etching of stainless steel has been already widely described in the literature using various agents and techniques [11–18]. Etching can be applied for revealing the microstructure of duplex type of steel by use of different agents such as 20% NaOH (used after heat treatment of steel up to 1300 °C) and 3 mol L^{-1} HCl (electrochemical etching at 300 mV vs SCE) [12]. In mixture of 2 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} HCl or in 1.5 mol L^{-1} HNO_3, by holding the potential at a fixed value corresponding to the dissolution of one of the phases, it is possible to reveal the microstructure of austenite (etching at 320 mV vs SCE) or ferrite (etching at 245 mV vs SCE) phases of steel [13]. For improving the adhesion of different type of coatings, stainless steel 316L has been etched either by cathodic sputtering [14] or by use of a "piranha" solution composed of sulphuric acid and hydrogen peroxide (H_2SO_4:H_2O_2 v/v 2:1) [15]. The surface roughness of commercially available nails was developed by use of the "piranha" solution, and the adhesion of a polymeric layer coating on the etched surface could be improved. Stainless steel 316L has been etched by an argon beam to create the base for coating with diamond like carbon (DLC) and to improve its physico–chemical properties, especially its biocompatibility [15]. For DLC coatings of thickness 400 μm, there is an optimal etching time of 15 min, beyond which the adhesive properties decrease.

Related with our objective, the works which concern the chemical fabrication of micro-channels and pits are the most relevant [16–18]. The effect of different agents ($FeCl_3$, HCl, HNO_3, $CrCl_3$) and their combinations, as well as temperature, on etching of stainless steel 301 has been deeply investigated [16]. HCl enhances the etching rate and HNO_3 is necessary for obtaining uniform channels, while $CrCl_3$ does not noteworthy influence the etching process. The pits growth and its correlation with temperature and chloride concentration at different stages of etching has been more carefully examined [17]. The conclusion is that the number of nucleation sites increases with chloride concentration, resulting in etching or delamination of the outer samples surface. The most informative is the work of Torchio et al. [18] where the influence of different ions (Cl^-, NO_3^-, Fe^{3+}, Al^{3+}) concentration on the etching mechanism is shown step by step as a function of temperature and type of steel. The Al^{3+} and Cl^- ions enhance the etching aggressiveness, whereas the Fe^{3+} ions have two properties: i) passivation of steel surface; ii) increase of pit growth when their concentration increases. NO_3^- and H_2O have inhibiting properties, especially NO_3^- ions are necessary to obtain uniform pits [17]. In all papers, it is shown that the etching rate increases with temperature, which is in agreement with a chemically activated process.

Accordingly to this literature review, we have selected a mixture of two compounds in order to favour an uniform spreading of pits on the surface of stainless steel: hydrochloric acid (HCl) for Cl^- anions which are responsible for creating nucleation sites and nitric acid (HNO_3) for NO_3^- anions which inhibit etching and allow uniform pits to be created. The modification of stainless steel surface has been imaged by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Capacitor electrodes have been manufactured by coating etched and non-etched stainless steel with activated carbon (AC). Impedance spectroscopy and cyclic voltammetry have been used to evaluate the electrochemical performance of AC/AC capacitors based on the etched collectors in 1 mol L^{-1} Li_2SO_4 and to demonstrate a noticeable improvement as compared to identical systems based on non-etched stainless steel.

2. Experimental

Commercially available stainless steel AISI 301 of thickness 15 μm from Inter-Belts (Poland) was used; this grade has been selected because etching can be performed in milder conditions than for e.g., steel 316L. The elemental composition of steel 301 was certified by the producer as follows: C – 0.11 wt.%, Si – 1.20 wt.%, Mn – 1.12 wt.%, P – 0.026 wt.%, S – 0.001 wt.%, Cr – 16.50 wt.%, Ni – 6.50 wt.%, Fe – 74.50 wt.%. The stainless steel samples were treated by a mixture of hydrochloric acid (35–38% Pure, Avantor) and nitric acid (65% Pure, Avantor). The mixture has been diluted with deionized water ($pH = 7$ and $\sigma = 0.5$ μS cm^{-1}) to a volumetric ratio in the range 1:3:20–50 (HNO_3: HCl: H_2O); in all cases, the pH of the solution was close to 1. The size of the samples used for etching varied from 4 cm^2, for preliminary understanding of the etching process, to 150 cm^2 on which the electrode material could be coated.

The foil was firstly degreased with 0.5 mol L^{-1} sodium hydroxide (Pure p.a., Chempur). Etching was done by placing the foil horizontally at the bottom of a rectangular polypropylene (PP) container. The volumes of etchant were 5 mL and 150 mL for 4 cm^2 and 150 cm^2 foils, respectively, in order to keep the same height of solution above the stainless steel foil. One side of the foil was in direct contact with the etching solution, while the other side was protected from etching by covering with a protective polymeric adhesive film, which could be easily removed at the end of the etching process. Etching was performed during 5–60 min under continuous stirring, using four magnetic rods placed in the corners of the container, without direct contact with the foil. After etching, the foil was rinsed with deionised water and sonicated for 15 min in order to wash out anchored impurities. The treated foil surface was further passivated with 10 wt% citric acid, $pH = 4$ (monohydrate, Pure P.A., Avantor) solution in water under stirring at around 50 °C for 1 h to remove iron (III) oxide [19,20]. After that, the foil was rinsed with water and once again sonicated for 15 min and then dried. The mass loss caused by etching was determined by measuring the mass of the foil prior and after etching. Small samples of 1 cm^2 were cut for SEM (Jeol JSM-7001F TTLS) and AFM (Agilent 5500 AFM) investigations.

The electrode material with composition 83.5 wt.% activated carbon (AC, DLC Supra 30, Norit, $S_{BET} = 2066$ m^2 g^{-1}, $D_{90} = 13$–20 μm), 8.0 wt.% binder (PVdF 5130, Solvay) and 8.5 wt.% of carbon percolator (Super C65, Timcal) was dispersed in 1-methyl-2-pyrrolidinone (NMP, 99.5% anhydrous, Sigma Aldrich) by use of an homogenizer (T18, IKA). The so-formed slurry was spread onto the surface of etched and as-received foils with use of an automatic film applicator (Elcometer 4340) and a doctor blade add-on with gap size 150 μm. NMP was then evacuated from the coatings by natural evaporation in air at 70 °C overnight and further under continuous vacuum at 120 °C for 15 h. After drying, the density and adhesion of coating was