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The modified activated carbon treated with a low-temperature iodine plasma used as electrode material for electrochemical capacitors

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ABSTRACT

This paper discusses a positive effect, of low-temperature plasma iodine treatment of activated carbon that could be used as electrode for electrochemical capacitor. The surface structure of the iodine-doped carbon tissue was examined using X-ray photoelectron spectroscopy (XPS). The surface area, and the carbon structure were characterized using gas adsorption method and observed by Scanning Electron Microscopy (SEM). The modified activated carbon material was used as electrode material of an electric double layer capacitor. The electrochemical characterization was carried out using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The electrochemical measurements confirmed an enhancement of the capacitance value after low-temperature iodine plasma treatment. The unusual behaviour of carbon/iodine interface is assumed to be related to redox activity of iodide-based species with various oxidation states from (−1) to (+5).

1. Introduction

Electric double-layer capacitors (EDLC) accumulate electric charge mainly by reversible electrostatic adsorption of ions in an electric double layer. Electrochemical capacitors are able to deliver the energy at high power rate, thus they fill the gap between the batteries and the conventional dielectric capacitors. Taking into account that the energy delivered by capacitor depends on the capacitance and applied voltage, it is reasonable to work on a high capacitance electrode materials and electrolytes with wide electrochemical stability [1–3].

The electrode capacitance can be enhanced significantly by using additional faradaic reaction as a source of the so-called pseudocapacitance. This phenomenon might be realized by exploitation of transition metal oxides (RuO_2, MnO_2, V_2O_5, SnO_2, Fe_3O_4 etc.), conducting polymers (polyaniline, polypyrrole) and by incorporation of heteroatoms (O, N) into carbon structure [4–8].

It is worth mentioning that the quick faradaic reactions as a source of pseudocapacitive phenomenon may originate from electrolyte solution. This effect was reported by Lota et al. [9]; as stated there, an aqueous solution of 1 mol L^{-1} KI plays a role of ordinary ionic-conductive electrolyte but also enhances the capacitance value of positive electrode because of various oxidation states of iodine from (−1) to (+5) [10,11].

Plasma treatment is one of the methods used to modify the carbon structure, either on chemical or physical manner. Physical treatment changes carbon surface area and pore size distribution. On the other hand, the chemical modification by oxygen plasma treatment remarkably influences oxygen functionalities on the carbon surface [12,13].

A number of papers reports on iodine-doping which changes a variety of carbon properties [14,15], but iodine plasma treatment has never been discussed. In this work the effect of iodine-doped activated carbon tissue done by low-temperature plasma treatment is discussed; this material was used as electroactive material for electrodes in EDLC.

2. Experimental

Commercial activated carbon material in the form of tissue Kynol 2000 from Kynol® Germany (labelled as K0) was used as raw material. Plasma processing was performed using a capacitively-coupled, low pressure reactor with radio frequency (RF, 13.56 MHz) glow discharge, described in details in reference [13]. Carbon tissue (5 cm × 5 cm) was used as a substrate. Iodine vapor

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(from solid iodine in 25 °C, 99.8%, Sigma-Aldrich) was used as plasma treatment precursor. Plasma process parameters were as follows: power of discharge – 20 W (labelled as K-I 20 W 10 m) and 80 W (labelled as K-I 80 W 10 m), treatment time – 10 min, operating pressure – 20 Pa. Plasma reaction chamber was filled in the iodine vapor from initial pressure 0.5–20 Pa, then the pump was cut off and at the same time the plasma treatment process was started. A scanning electron microscope (SEM EVO® 40 ZEISS) was used to observe the structure of the materials. The BET specific surface area was determined from N_2 physisorption at 77 K (Micromeritics ASAP 2010). The XPS technique was applied to determine the surface chemical structure using AXIS Ultra spectrometer (Kratos Analytical Ltd.) equipped with monochromated Al Kα X-ray source (1486.6 eV). The power of anode was set at 150 W and the hemispherical electron energy analyzer was operated at a pass energy 20 eV for all high resolution measurements.

All electrochemical measurements were carried out with two- and three-electrode cells assembled in a Swagelok® system using tissue carbon material (before and after plasma treatment) as electrode material (12–16 mg, 0.8 cm^2) in pH-neutral, aqueous solution of 1 mol L^{-1} Li_2SO_4 (≥ 99.0%, Sigma-Aldrich). The capacitance properties (expressed per mass of a single electrode) were studied by galvanostatic charge/discharge 100–10,000 mA g^{-1}), cyclic voltammetry at scan rates from 5 to 100 mV s^{-1} and electrochemical impedance spectroscopy (EIS) from 100 kHz to 1 mHz using potentiostat/galvanostat VMP3/Z Biologic (France).

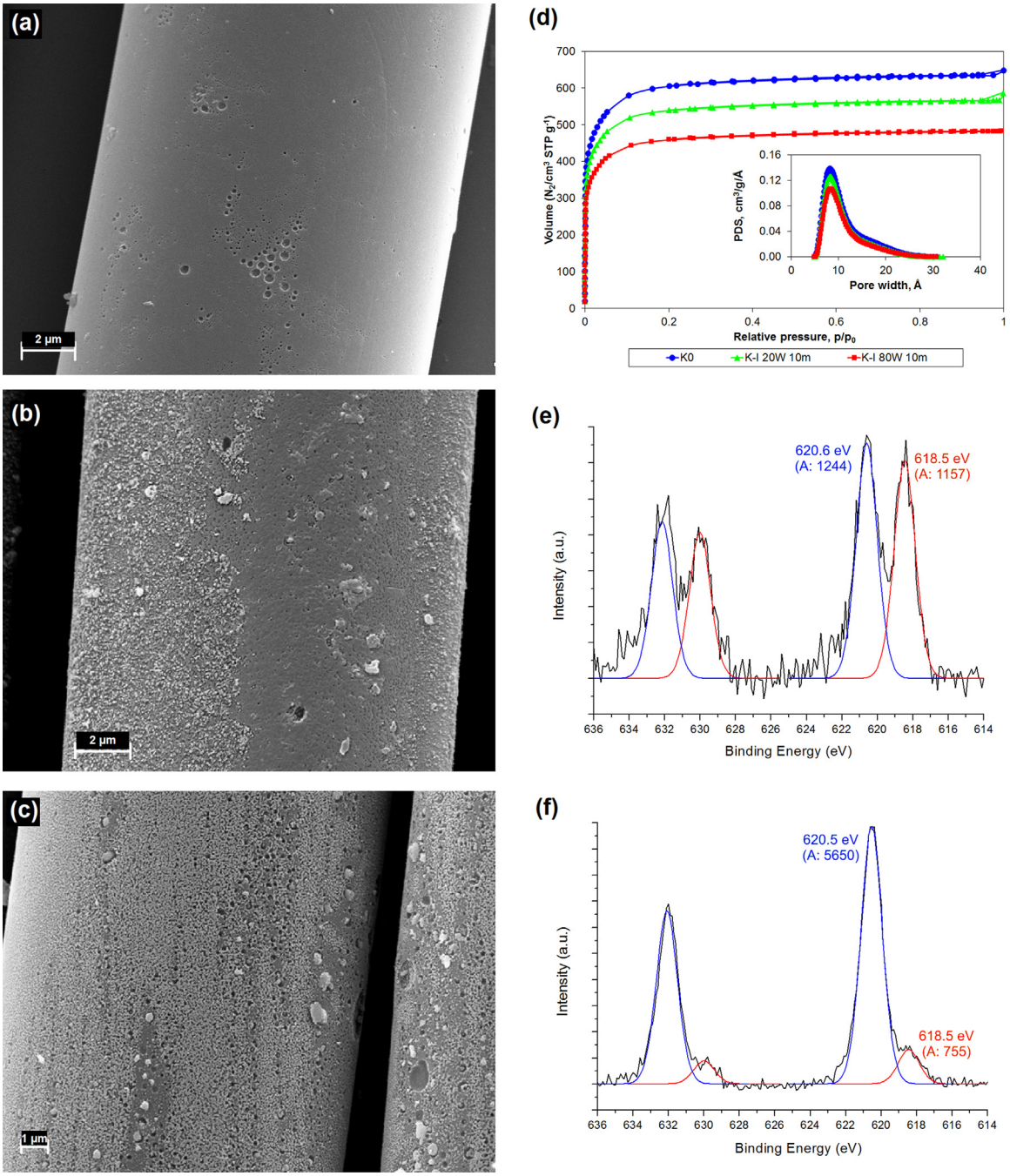

Fig. 1. SEM images: of unmodified carbon tissue (K0) (a); K-I 20 W 10 m (b) and K-I 80 W 10 m (c); Nitrogen adsorption/desorption isotherms at 77 K; inset: pore size distribution (d); XPS spectrum of I 3d line for K-I 20 W 10 m sample surface (A – under-peak area (cps × eV)) (e); XPS spectrum of I 3d line for K-I 80 W 10 m sample surface (A – under-peak area (cps × eV)) (f).