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Can conductivity measurements serve as a tool for assessing pseudocapacitance processes occurring on carbon electrodes?

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Abstract

The dependence of the electronic conductivity of carbon electrodes on their potential while being immersed in acidic solutions was studied. The precursors for the carbons studied were Kapton polymer, cellulose, and cellulose that was carbonized in the presence of ammonium chloride (at 1000 °C), followed by a mild oxidation process (CO_2 at 900 °C) for various periods of time, in order to obtain carbons of large specific surface areas. Unlike the case of neutral electrolyte solutions, which show a parabolic dependence of the carbons' conductivity on the electrodes' potential, the dependence of the conductivity on the potential of carbon electrodes immersed in HCl solutions exhibits inverted parabolic-type dependence. Carbons of different surface chemistry were prepared in order to determine the main cause for this unusual behavior. It was found that when nitrogen heteroatoms are present in the carbons' structure, pseudofaradaic reactions occur, causing this phenomenon. When the nitrogen-containing functional groups on the carbon surface undergo redox reactions, the conjugated system adjacent to these nitrogen atoms changes and the carbon system loses highly conductive electronic arrangements. Therefore, upon the anodic or cathodic polarization of nitrogen-containing carbon electrodes, the nitrogen-containing groups are oxidized or reduced, respectively, and the electronic conductivity of these electrodes decreases accordingly.

Keywords: Carbon electrodes; Electronic conductivity; Surface chemistry; Pseudocapacitance

1. Introduction

The dependence of the electronic conductivity of molecular sieve carbon electrodes on their potential, while being immersed in electrolyte solutions, was recently studied [1]. When the pore size is sufficiently large to accommodate anions and cations, the classic curve shape of this type of measurement is a parabolic dependence of the conductivity on the electrode's potential [2], with a minimum at the potential of zero charge (PZC). However, when the average pore size of carbon electrodes approaches the size of the cations or the anions in the solution (i.e. the ions cannot enter the pores), the electrode's conductivity was found to be nearly potential invariant in the potential range where electro-adsorption is not pronounced. Efficient electro-adsorption (i.e. the pores are large enough to allow the insertion of ions) enables the neutralization and stabilization of the excess charge near the carbon's surface (electrode's side) by the electro-adsorption of ions in the solution side of the interface. This enables an accumulation of charge near the electrode's surface, and hence, leads to an increase in electrical conductivity. Therefore, when the pore size of the carbon electrodes does not allow ion electro-adsorption upon polarization of the electrodes, electrons or holes cannot be stabilized in the solid side of the interface. Thereby, the electronic conductivity of the electrodes remains constant as a function of the applied potential.

In a previous study [3], an unusual behavior was reported for carbon electrodes of large pore sizes that were polarized in KCl solutions of high concentration. Instead of the expected parabolic shape of the conductivity vs.

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potential curves, cubic parabolic curves are obtained. This behavior relates to the formation of H^+ ions during the polarization of the carbon electrodes [4]. H^+ ions thus formed are electro-adsorbed to the carbon electrode's surface, thus widening the potential domain of the cations' electro-adsorption. As a result, no minimum is observed in the conductivity vs. potential curves measured with these systems.

Reversible redox reactions of surface groups are known to increase the capacitance of carbon electrodes in acidic media. These reactions, termed as pseudocapacitance reactions [5], involve heteroatoms such as oxygen [6] and nitrogen [7,8] containing groups on the surface of the carbon electrodes. These reactions are usually characterized by classical electrochemical methods such as CV (cyclic voltammetry) and impedance spectroscopy [9]. In this study, the dependence of conductivity on the potential of carbon electrodes in acidic media was studied. It was determined that carbons containing nitrogen as part of their structure behave quite differently from nitrogen-free carbons. Such measurements can serve as an additional tool for assessing pseudocapacitance reactions related to nitrogen heteroatoms on the surface of carbon electrodes.

2. Experimental

Cellulose-based carbon originating from cellulose films (Goodfellow Inc.) was produced via two different preparation procedures: (a) temperature-programmed pyrolysis (heating rate of 2 °C/min, up to 1000 °C) under a nitrogen flow (99.999% purity, Oxygen & Argon Works, Israel), in the presence of ammonium chloride (Aldrich Inc.), 10% by weight; (b) by the same procedure as in (a), without ammonium chloride. Kapton-based carbons, originating from Kapton polymer films (Pronat Israel, Inc.) were produced by temperature-programmed pyrolysis (heating rate of 2 °C/min, up to 1000 °C) under a nitrogen flow. The carbonaceous products thus obtained, regardless of the precursor used, possessed a negligible specific surface area (BET), which corresponded mostly to the external geometric surface area of the carbons. The activation of the carbonized samples was performed by CO_2 (99.995% purity, BOC Gases) at 900 °C during various periods of time. Carbons with surface areas of several hundreds of square meters per gram were obtained by this activation method.

In order to determine the effect of oxygen-containing surface groups, two types of further activated Kapton-based carbons were produced. The first type underwent chemical activation, in order to form carbons enriched with surface groups, by dipping the carbon samples in nitric acid solutions (60% w/w in water) [10] for 0.5 h at RT. The second type of carbon samples underwent a chemical reduction process in order to reduce the content of oxygen-containing groups from the carbon surface at 900 °C under Ar/H_2 flow (95%/5%, Oxygen & Argon Works, Israel) for 1 h [10]. These samples were then stored under high-purity argon in a glove box (M. Braun, Inc.) in order to prevent the reformation of surface groups in the presence of oxygen from the air.

The experimental set up for measurements of the electronic conductivity of carbon electrodes in solutions as a function of their electrochemical potential has already been described in detail [1]. Prior to each conductivity measurement, the potential was scanned (1 mV/s) from the immersion potential to −0.4 V vs. SCE (saturated calomel electrode). A period of at least two hours was required at each potential in order to ensure that the electrochemically-induced current of the carbon electrode is negligible in comparison with the source current used for the conductivity measurement. The carbon electrode conductivity was measured at an electrochemical potential range of $-0.4\ \text{V} \rightarrow +0.6\ \text{V}$ vs. SCE, with intervals of 100 mV.

Cyclic voltammetry of carbon electrodes, measured by a PGSTAT Autolab electrochemical measuring system from Ecco Chemie, Inc., The Netherlands, was performed at a scan rate of 1 mV/s at a potential range of −0.4 V and 0.7 V vs. SCE. Prior to each conductivity measurement, the carbon electrodes were cycled at the above-mentioned potential range, until steady and repetitive voltammograms were obtained. The electrodes' capacity was calculated from the cyclic voltammograms, using the relation C [F/g] = (I/v)/electrode mass [g], where I is the current in amperes and v is the scan rate in V/s.

Adsorption isotherms and surface area measurements were obtained by an Autosorb 1 system (Quantachrome Inc.) using nitrogen as an adsorbate at 77 K.

Surface analysis of the carbons by photoelectron spectroscopy (XPS) was performed with a Kratos AXIS-HS spectrometer, using a monochromatic Al Kα source (1486.68 eV). All binding energies were calibrated to a C1s graphitic peak position at 285 eV.

The salts for the electrolyte solutions were obtained from the following companies: KCl from Frutarom (Israel) and HCl from Bio-Lab (Israel). Doubly-distilled water was used for the preparation of all the electrolyte solutions.

3. Results

Specific BET surface areas of the differently treated carbon samples (thermally activated and chemically activated by CO_2 at 900 °C and by HNO_3 solution, respectively) are shown in Table 1. A decrease in the BET surface area was observed after dipping the activated carbon samples in an

Table 1
BET surface area of the different carbon samples

Carbon sample	Activation type	BET surface area (m^2/g)
Cellulose	1 h CO_2	270
Cellulose + NH_4Cl	1 h CO_2	140
Kapton	4 h CO_2	440
Kapton	4 h CO_2 + 30 min HNO_3	410
Kapton	4 h CO_2 + 1 h Ar/H_2 900 °C	465