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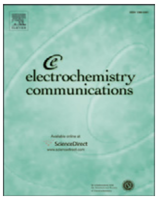

Proton-selective electrode for pH sensing

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ABSTRACT

Cellulose-based carbon electrodes with pores of different widths (~2.6 and ~4 nm) have been fabricated by the pyrolysis of cellulose filter paper, followed by mild activation and surface treatment in nitric acid. Such electrodes were introduced into solutions with different pH values and their potential was measured vs. a reference electrode. Nernstian behavior between measured potentials and solution pH with a slope value of 57 mV per decade was only demonstrated for the carbon with the smaller pore size. This carbon also has proton-selective properties, unlike the carbons with wide pores. Based on the modified Donnan model of the electrical double-layer structure, it is hypothesized that the micropores of proton-selective carbons can hold a fixed amount of protons, regardless of the composition of the solution outside the micropores, when a Donnan potential between the carbon-electrode micropores and the external solution is established.

1. Introduction

1.1. Common methods for pH sensing

Sensors that detect pH levels are widely used in many applications, such as laboratory pH measurements, environmental monitoring and biomedical applications [1–4]. Acidity can be measured by chemical indicators, such as litmus paper that changes its color according to the pH of a solution [5]. The most widespread technique to measure pH, due to its high selectivity toward protons, is by glass membrane electrodes [6, 7]. Potentiometric pH sensing based on ion-selective electrodes can be a good choice, because it provides an economical and simple way for pH monitoring. Optical and fluorescent sensors, which are based on pH-dependent changes of the absorbance or luminescence of an indicator molecule [8–10], have recently been developed specifically for biomedical applications [11–13]. The possibility to sense pH with surface-modified carbon materials has been studied extensively [14–16]. Oxygen-containing groups such as quinone may behave, at the edge plane sites of such carbon electrodes, as electrochemically reversible redox couples that interact with protons. Such redox interactions may, indeed, provide the basis for potentiometric pH sensing.

1.2. Proton-selective electrodes

The electro-adsorption capacity of porous carbon electrodes is usually a function of their surface area. It is possible to control the pore-size distribution and micropore content in porous carbon electrodes by applying various activation procedures, all of which are essentially controlled burn-off processes by oxidizing agents, which increase the surface area and pore size of carbonaceous materials [17–21].

In a previous publication [22], it was shown that carbons (originating from phenol-formaldehyde cloth) with ultramicropores and oxygen-containing functional groups show complete rejection of anions. The anion repulsion was attributed to a combination of the molecular-sieving effect of these electrodes and charge-dipole interaction. When the pores are too small, yet larger than the anionic dimensions, there is repulsion of anions from the surface C═O dipoles.

In other publications [23,24], it was shown that protons have a different electro-adsorption mechanism than other ions, which cannot be attributed solely to the pore-size distribution of the carbon. Followed by consistent experimental work, it was hypothesized that, unlike other ions, hydrated protons can be stripped of most of their hydration sheath upon electro-adsorption into small pores a few Å in diameter. Such interactions between ions and carbon walls in sub-nanopores are not possible with regular ions, thus leading to the high electro-adsorption stereo-selectivity of H_3O^+ over other ions.

By controlled activation, a precise pore-size distribution can be obtained with activated carbons in the order of a few angstroms. The surface of the carbon can be modified, for instance, by oxidation using concentrated aqueous HNO_3 solutions [25]. For the case of low-surface carbon, such an oxidation can increase the surface area and also introduce oxygen-containing functional groups. However, it is also possible by such treatment to increase the surface area of the carbon without the massive formation of oxygen-containing surface groups [25].

Here, we demonstrate that by tuning the pore size of the carbon with liquid HNO_3, a molecular sieving effect toward proton adsorption can be

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achieved. The proton molecular sieving carbons can be used for the potentiometric determination of solution pH, as shall be described.

2. Experimental details

2.1. Materials

Analytical-grade NaCl (greater than 99%) was purchased from Frutarom, Israel. HCl (36%) and HNO_3 (70%) were obtained from Sigma-Aldrich. Buffer solutions were obtained from Hanna Instruments, Inc. The precursor for the carbon material was cellulose filter paper (Whatman Inc.). The carbon papers were produced by temperature-programmed pyrolysis under argon flow. The temperature program included a slow ramp of 0.58 °C/min in the 150 to 400 °C range, and then an increase of 18 °C/min from 400 to 600 °C. Activation of the carbon paper was achieved with an aqueous HNO_3 solution at room temperature by dipping carbon-paper samples into the HNO_3 (70%) solution for various time durations.

2.2. Electrochemical measurements

Simple three-electrode cells were used. The electrodes were attached to platinum current collectors. Highly porous carbon served as the counter-electrodes. The reference electrodes, placed adjacent to the working electrodes, were standard saturated calomel electrodes (SCE).

The electrochemical measurements (cyclic voltammetry (CV)) were conducted with a PGSTAT Autolab electrochemical measuring system from Ecco Chemie, Inc. The capacitance was calculated from the current values of the voltammograms according to $C = I/(dV/dt)$, where I is in amperes per gram of electrode material, V is the electrode potential in volts, t is the time (in seconds) and C is the capacity magnitude in farads per gram.

Potentiometric voltage recording between the carbon electrodes and reference electrodes was performed with a standard multimeter (Lutron DM-9680).

2.3. Adsorption measurement

A Gemini 2375 Micromeritics analyzer was used to measure nitrogen adsorption isotherms at 77 K. The pore-size distributions were determined using density-functional theory (DFT).

3. Results and discussion

3.1. Acidic and basic ionizable surface groups

The surface oxides on carbons can have acidic and basic properties. Acidic functional surface groups can include carboxylic, phenolic, lactonic and carbonyl surface groups.

To demonstrate this, let us assume that the deprotonation of the carboxylic groups is

$$\mathrm{C{-}COOH + H_2O \Leftrightarrow C{-}COO^- + H_3O^+}. \tag{1}$$

Usually, acidic surface groups are formed by the reaction of carbon with oxygen at a high temperature or with a liquid oxidant. The acidic surface groups have cation exchange properties. The degree of protonation of the acidic surface functional groups is a function of carbon physicochemical properties such as the shape of the poly-aromatic layers and the surrounding environment in contact with the carbon surface [26–29].

3.2. From a classical description of the solid-water interface of ionizable surfaces to proton-selective electrodes

3.2.1. Solid-water interface of ionizable surface

The following equations are an example of the classical solid-water interfaces of ionizable surfaces in the presence of 1:1 monovalent ions (not restricted to porous media) [30,31].

Let us assume that only protons can bind to a negatively charged carbon surface, which is a reasonable assumption, taking into account the selectivity properties of the electrodes within the micropores. The equilibrium is given by

$$S_0^- + H_0^+ \Leftrightarrow [SH]_0, \tag{2}$$

where S_0^-, H_0^+ and $[SH]_0$ represent the concentration of the dissociated sites, protons and undissociated sites at the surface, respectively.

The surface dissociation constant K_d is given by

$$K_d = \frac{[S^-]_0[H^+]_0}{[SH]_0}. \tag{3}$$

The proton concentration $[H^+]_0$ at the surface can be expressed by the Boltzmann relation

$$[H^+]_0 = [H^+]_{bulk} e^{\frac{-q\phi_0}{kT}}, \tag{4}$$

where ϕ_0 is the surface potential, $[H^+]_{bulk}$ is the molar concentration of protons in the bulk, q is the elementary charge, k is Boltzmann constant and T is the temperature (in Kelvin).

The surface-charge density can be expressed in terms of the dissociated surface group sites by

$$\sigma_I = -q[S^-]. \tag{5}$$

Proceeding with this classical description of the water-solid interface of the ionizable charged surface, we assume that the surface potential is identical to that of the diffuse layer potential (in other words, $\phi_0 = \phi_D$). Making this assumption enables us to express the inner charge-potential–concentration relationship in terms of the average diffusion-layer potential ϕ_D. Because the surface concentration of the ionizable sites $[S^*]$ remains constant, $[S^*] = [S^-]_0 + [SH]_0$. Combining Eqs. (3)–(5) leads to.

$$\sigma_I = q[S^*]\frac{[H^+]_{bulk}}{[H^+]_{bulk} + K_d e^{\frac{q\phi_D}{kT}}}. \tag{6}$$

Note that the description above is not new. It is well referenced and serves as an important introduction to the main theme of this paper.

These equations attempt to describe the inner-layer charge as a function of the surface or average diffusion-layer potential. They imply that both the surface potential and the surface-charge density should vary with changes in the pH values of the bulk electrolyte solution.

In practice, the average diffuse layer potential and surface-charge relationship between the ionizable charged surfaces are not solely dependent on the pH. The electrolyte solution ionic strength plays a significant role in determining these parameters. Trefalt et al. [30] have shown an inverted dependence of the potential on the electrolyte ionic strength at a given pH, where, in their work, the interface was charged by ionization with amine groups (weakly basic groups) at various pH values. They showed that the potential increases with the decrease in the ionic strength, whereas the surface charge increases. They explained this as follows: when the ionic strength increases, the interactions between the ionizable sites are screened and the electrode surface can adsorb an increasing number of protons. Consequently, the inner surface charge grows, and the charge accumulates closer to the surface and effectively lowers the surface potential. However, the surface charge and