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ELABORATION AND ELECTRICAL CHARACTERIZATION OF SENSORS FUNCTIONALIZED BY ANION-EXCHANGING MATERIALS

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ABSTRACT: Anion exchange phenomena inside various functional coatings have been investigated by means of impedance measurements. Emphasis is given to the selectivity of anions that would allow the application to ion-selective electrodes based on electrolyte/insulator/semiconductor devices. The selectivity of anion exchange with respect to anion type follows the empirical Hofmeister sorting series. But other parameters are also operating such as the chemical nature of the anionic sites and the possible anion-dependent swelling of the electrode's coating by the solvent.

Keywords: anion exchange, ion selectivity, impedance measurements

RÉSUMÉ : Les phénomènes d'échange anionique dans divers revêtements fonctionnels ont été étudiés au moyen de mesures d'impédance. L'accent est mis sur la sélectivité des anions qui permettrait l'application d'électrodes sélectives d'ions basées sur les dispositifs : électrolyte / isolant / semi-conducteur. La sélectivité de l'échange d'anions par rapport au type d'anions suit la série empirique de Hofmeister. Mais d'autres paramètres sont également présents tels que la nature chimique des sites anioniques et le gonflement possible du revêtement d'électrode par le solvant qui dépend de la nature de l'anion.

Mots clés : échange anionique, sélectivité ionique, mesures d'impédance

1. Introduction

The elaboration of ion-sensitive sensors requires a suitable surface chemistry of the transducer for the electrochemical signal which is measured to be dependent of the target ions concentration [1,2]. The detection of anions for an analytical purpose can be obtained by means of the chemical recognition of the ion to be analyzed at the functionalized surface of the transducer [3]. This is achieved either their selective complexation to a neutral ionophore, or an anion exchange phenomenon inside an ion-exchanging material where the anion of the background electrolyte is replaced by the target anion that binds strongly to the surface sites [4-6]. In both cases, the surface of the transducer is chemically modified so as to make it sensitive to the ionic species [7,8]. The present case, the detection mode relies on anion-exchange phenomena at the surface of electrodes immersed in an electrolyte solution. Several questions that are addressed concern the mechanism of the anion exchange itself, the origin of the selectivity of the anion exchange and the relationships between the anion exchange and the electrical signals that the electrochemical device allows measuring. Thus, the silica surface of semi-conducting silicon electrodes has been sensitized towards the presence of anions by coating the surface of the transducer with a polymer film where the anion exchanges take place.

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A cationic polymer deposited as a thick film allows anion exchange phenomena to take place close to the silica surface, giving rise to an electrical signal revealed by impedance measurements. The electrolyte/insulator/semiconductor electrochemical system allows the measurements of the electrical characteristics of the anion exchange phenomenon as a function of the anion concentration. Such a device allows a detailed investigation of the microscopic mechanisms of ion exchange and to optimize the surface chemistry in view of a future transposition to sensors based on more robust and fast devices such as ISFET's. The variation of the flat band potential of the EIS system as a function of the anion concentration is of particular relevance with that respect.

The binding of ions to electrically charged sites depends not only on electrostatic interactions but also on several "specific" interactions providing selectivity to ion binding, even for ions having the same electrical charge. The selectivity has various origins such as hydration energies of the ions, dispersion interactions, such interactions not being completely elucidated yet. The binding of anions on different types of membranes has been investigated so as to discuss the molecular interactions which are responsible for the anion selectivity. The specificity of ion exchange phenomena in polymer membranes has deserved much attention in the domain of ion-selective electrodes where a self supported polymer membrane separates the analyte solution and a reference solution compartment [9]. In the classical case, an ionophore and a lipophilic electrolyte are dissolved or dispersed inside polymer materials, most often plasticized PVC [10-12]. Ion-exchange is involved in the case of ion-pair ionophores such as the lipophilic quaternary ammonium molecules used for instance in the manufacture of chloride-selective electrodes [13,14]. On the contrary, the polymer films deposited at the surface of electrodes are been less studied and the issues are different in many instances because the materials are not the same (functionalized polymers can be used, films are thinner) and the measured electrical parameters are not sensitive to the same microscopic phenomena.

Anion exchange membranes have been elaborated as thin films of cationic species on Si/SiO_2 substrates allowing electrochemical measurements to be carried out. Two different types of membranes have been investigated, which are representative of the two main technologies of electrode sensitization by means of grafting organic materials. The first type of coating is made of a thin layer of quaternary ammonium groups immobilized to the surface by means of a chemical grafting an organosilane. A thin cationic layer is formed, its thickness being of the order of a molecular size (~1 nm); the mechanism of ion binding is a 2-dimensional chemical recognition by means of adsorption to the cationic surface sites at a hydrophilic surface. The second type of membrane consists in a thick layer of cationic polymer deposited at the surface of the electrodes. The membrane thickness of ~100 nm makes the ion exchange phenomenon more complex since ions need to penetrate the hydrophobic membrane in order to reach the internal cationic site. The second type of membrane consists in a thick layer of cationic polymer deposited at the surface of the electrodes. The chemical recognition takes place in a 3-dimensional medium once the anions have entered the organic membrane material. The dependency on anion type may be different in both materials because the mechanisms of anion exchange are different.

The anion exchange between the membranes and aqueous solutions could be investigated by means of systematic impedance measurements as a function of anions concentration and type. From capacitance measurements as a function of applied potential, both the flat band potential ΔV_{FB} and capacitance in accumulation regime ΔC were extracted as relevant anion-sensitive electrical parameters (Figure 1).

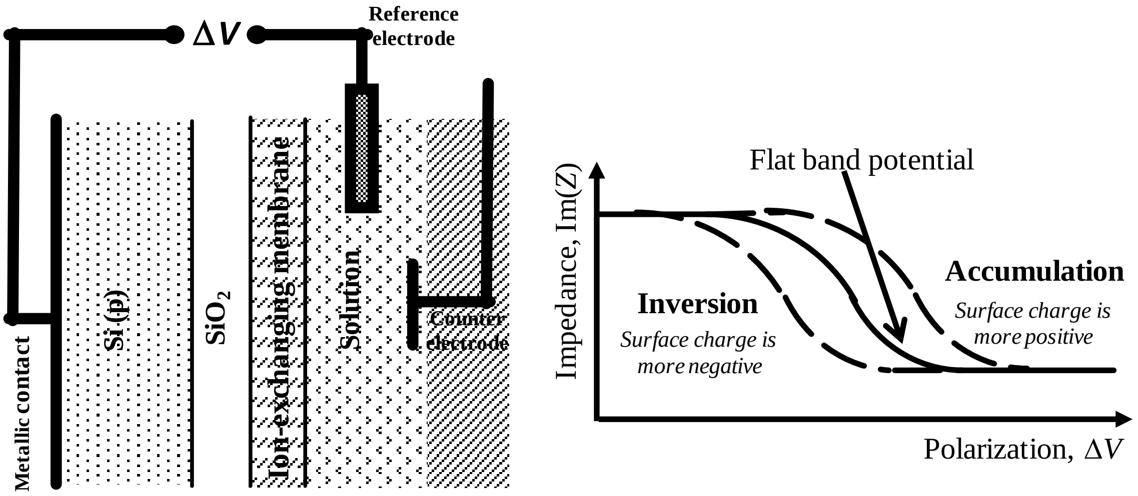

Figure 1: *Schematic measurement set up and capacitance variation against applied potential* Δ*V showing the inversion and accumulation regimes of the space charge in the semiconductor. Anion exchange shifts the Im(Z) vs* Δ*V curves according the ion type.*

2. Materials and methods

2.1. Materials

A first type of membrane was elaborated by deposition of cationic silicone based polymers bearing various anion exchanging groups: triethylammonium, pyridinium or triphenyl phosphonium [15]. A second material was prepared by means of an original sol-gel process by *in situ* polycondensation of an aminosilane, such as coupling agent, followed by functionalization with glycidyltrimethyl-ammonium chloride [16]. These two types of membrane are presented in Figure 2.

The layers of anion exchanging materials have been characterized by spectroscopic methods, electron microscopy, ellipsometry and atomic force microscopy AFM [15].

2.2. Electrochemical measurements

Anion exchange phenomena have been monitored by means of electrochemical measurements of impedance as a function of applied potential. An electrochemical cell equipped with a VoltaLab 40 impedance analyser and a three electrodes potentiostatic set up PGS 301 from Radiometer Analytical was used for measurements of a.c. capacitance at 10 kHz frequency and 10 mV amplitude of the alternating voltage signal. The counter electrode was a gold wire and the reference was a saturated calomel electrode. Out of phase impedance were recorded for bias voltages *V* varying from -500 to 2700 mV/SCE. Anion exchange took place between acetate anions and the various anions under study. The electrodes were equilibrated in the background electrolyte made of 10 mM sodium acetate at pH 6.8 before the various anions were added at increasing concentrations. The capacitance measurements as a function of the anion concentration were most often S-shaped, allowing analytical parameters to be extracted. Starting from low anion concentrations where the anion exchange is insignificant, increasing the anion concentration results in an increasing anion exchange and a subsequent modification of the electrical state of the polymer membrane revealed by the electrical measurements. The variation of the capacitance stops when the anion exchange has completed at high enough concentrations of anions in solution. Therefore, the full variations correspond to full anion exchange.

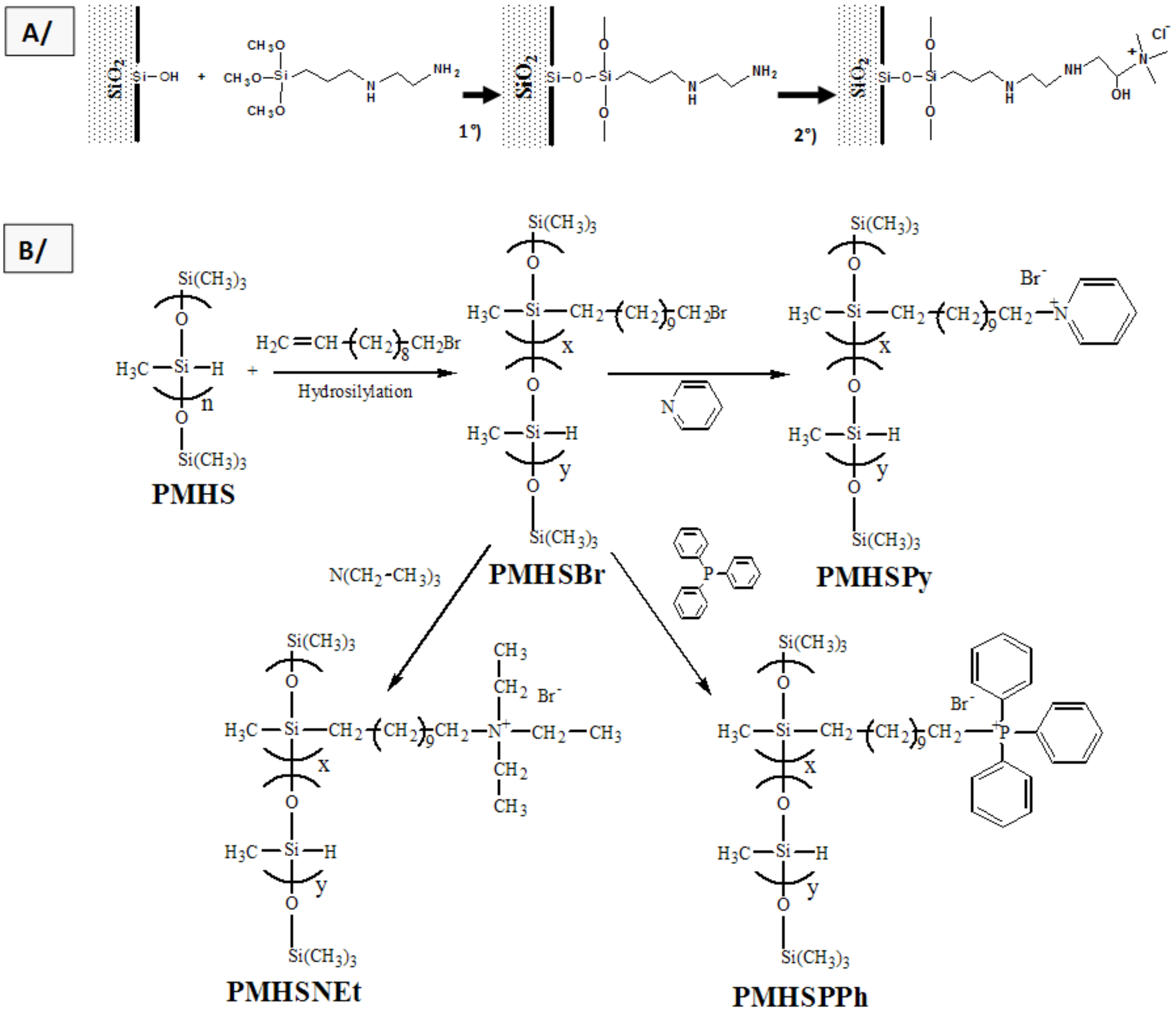

Figure 2: ***A/*** *Synthesis of a* ***hydrophilic membrane*** *bound to a Si/SiO*$_2$ *electrode by a sol-gel process: Step 1°) the trimethoxysilane forms a layer of polycondensed silane by a sol-gel process in the presence of water; Step 2°) reaction between epoxy groups of glycidyltrimethylammonium chloride and amino groups of the grafted 3-(2-aminoethyl-amino)propyltrimethoxysilane [16].*
B/ *Synthesis of a* ***hydrophobic membrane*** *bound to a Si/SiO*$_2$ *electrode by in situ cross-linking a cationic silicone polymer: Step 1°) the polymethylhydrosiloxane PMHS was reacted with 11-bromo-1-undecene by means of a hydrosilylation reaction; Step 2°) the resulting polymer PMHSBr was converted into either PMHSPy, PMHSNEt or PMHSPPh by means of its quaternarisation reaction with pyridine, triethylamine or triphenylphosphine respectively [15]. The average polymerization degree of PMHS is n = 35; partial functionalization gives x = 10 and y = 25.*

One important parameter is the detection limit which is the minimum anion concentration that can be detected. The detection limit for different anions allows to discuss on the sensitivity of the electrochemical device to anion exchange phenomena; the lower the detection limit; the larger the affinity of the anion for the polymer membrane. The slope of the variation of the flat band potential with respect to Log(anion concentration) is a similar way to estimate the sensitivity; it is often compared with the prediction of the Nernst law. Electrical parameters such as the variation of the flat band potential ΔV_{FB} and capacitance ΔC upon full anion exchange condition are also relevant parameters. The determination various parameters from the capacitance measurements are summarized in Figure 3. Since the anion exchange involves substitution of acetate anions of the background electrolyte for the various added anions, the sensitivity is related to the selectivity with respect to acetate. The selectivity with respect to different anions is simply inferred from the differences of sensitivity (from the detection limit or slope) of different anions.

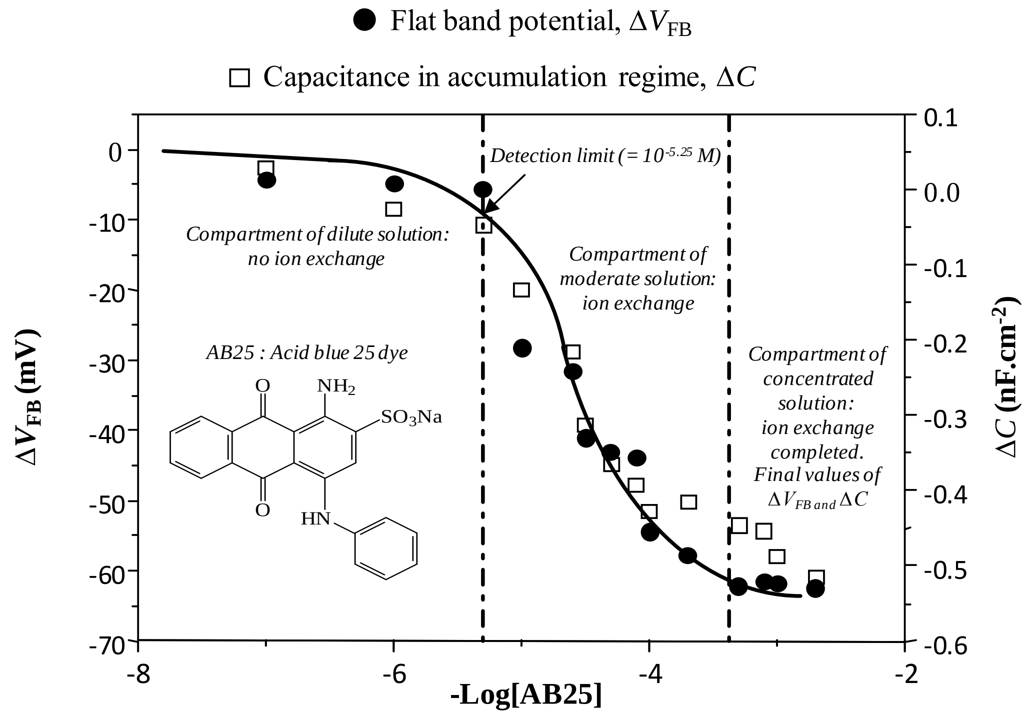

Figure 3: *Variation of the flat band potential upon anion exchange of acetate for AB25 dye on hydrophobic membrane PMHSNEt (cationic site $^{+}N(Et)_3$) bound to a Si/SiO_2 electrode showing the different regimes and the extracted analytical parameters.*

3. Results and discussion with respect to various anions and membranes

The selectivity of anion exchange was essentially found in the order of the lyotropic series of Hofmeister [17-19] in all cases: Acid Blue (AB25) > ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > F^- > $H_2PO_4^-$ > AcO^- (acetate). The anionic dye Acid Blue 25 binds the most tightly because of its strong hydrophobic character. The acetate anion is placed at the end of the series since full anion exchange could be achieved for all anions at concentration lower than that of the background electrolyte (10 mM AcO^-). However, there are some variations in the order for other ions according to the criterion that was used for sorting the ions (detection limit, variations of flat band potential or capacitance of the membrane). The main contribution to the flat band potential variation was the electrical double layer at the membrane-solution interface whereas ΔC was mostly affected by the anion exchange inside the membrane material.

The results obtained with polymers coating having different anion-exchanging groups showed ion-selectivity. Given an anion type, the electrical signal depends on the nature of the cationic group (triethylammonium, pyridinium and triphenyl phosphonium) attached to the same polymer, showing that the anion recognition is not only determined by the type of anion as the Hofmeister series would suggest, but also to the chemical nature of the host. The chemistry of the surface sites also matter. Combined with the several types of electrical measurements which are not sensitive in the same way to the anion concentration, the dependence on the host chemical nature opens the possibility for anion-selective measurements in case where the selectivity of one type of membrane is not favorable. Therefore, a set of several measurement types (ΔV_{FB}, ΔC) performed with several devices sensitized with different types of membranes might allow the determination of anion concentrations in complex mixtures (Table 1).

Table 1: *Electrical characteristic of the thick films (3D) of functional silicone material.*

Cationic site	Anion	Detection limit (M)	ΔV_{FB} (mV)	ΔC (nF.cm^{-2})
$^+N(Et)_3$	F^-	$10^{-4.4}$	-18	-0.06
	NO_3^-	$10^{-4.6}$	-23	-0.12
	I^-	$10^{-4.6}$	-45	-0.5
	$AB25^-$	$10^{-5.25}$	-60	-0.5
	SO_4^{2-}	$10^{-5.25}$	-13	-0.015
Pyridinium	I^-	$10^{-4.6}$	-42	-0.5
Phosphonium	I^-	$10^{-5.5}$	-37	-0.5

The electrical behavior of the very thin (2D) sol-gel material was quite different of those of the 100 nm thick (3D) functional silicone membranes. The selectivity still follows the Hofmeister series but the variations of ΔV_{FB} and ΔC suggest that the internal structure of the thin film strongly depend on the anion type. In particular, the swelling by water depends on the hydrophilic character of the anion (Figure 4) (Table 2). Swelling by water is limited by the size of the grafted molecules however, so that the variations of capacity ΔC were quite small compared to that in the thick 3D material.

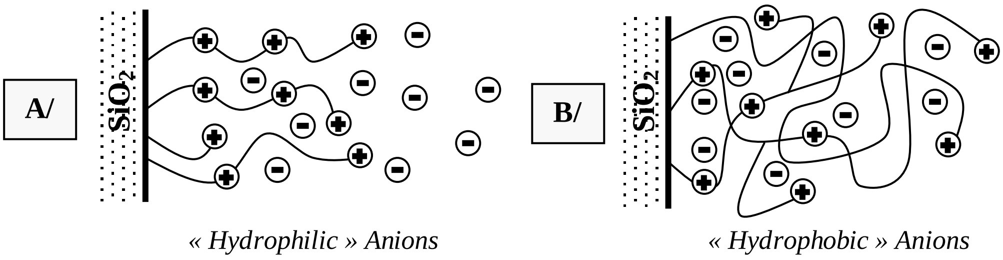

Figure 4: ***A/*** *Adsorption of hydrophilic anions on thin anion-exchange coating.* ***B/*** *Adsorption of hydrophobic anions on thick anion-exchange coating.*

Table 2: *Electrical characteristics of the thin films (2D) prepared by means of the sol-gel silane chemistry.*

Anion	Detection limit (M)	ΔV_{FB} (mV)	ΔC (nF.cm^{-2})
F^-	$10^{-4.0}$	-16	0.0
I^-	$10^{-4.5}$	-25	-0.05
$AB25^-$	$10^{-5.0}$	-23	-0.05

4. Conclusion

Ion exchange phenomena inside thin and thick polymer films can be investigated by means of electrochemical measurements on coated electrodes. The empirical Hofmeister series that usually describe the ion-specificity of various phenomena including ion-exchange and ion adsorption is still followed. But the phenomena do not solely depend on the anion type since the chemistry of the surface materials is also of major importance. The type and strength of interactions of anions with surface sites at a microscopic level provide are the first meaningful parameters. The dependence of physical properties of the coating on the nature of the anions provide another useful way for departing from the quasi-universal Hofmeister sorting series that limit the utility of anion exchange phenomena for selective detections of anions. The thin (2D) and thick (3D) membranes show up the same order of anion binding according to the Hofmeister series. However the magnitudes of the variations of electrochemical parameters upon full anion exchange (ΔV_{FB} and ΔC) are different for both electrical devices. Regarding the application to chemical sensors, each type of sensitive membrane requires a specific electrochemical measurement for optimum sensitivity of the ionic species detection.

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