



Sodium- and chloride-selective microelectrodes optimized for corrosion studies



Valentine A. Nazarov^a, Maryna G. Taryba^b, Elena A. Zdrachek^c, Kseniya A. Andronchyk^c, Vladimir V. Egorov^{c,*}, Svetlana V. Lamaka^b

^a Research Institute for Physical Chemical Problems, Leningradskaya Str., 14, 220030 Minsk, Belarus

^b Instituto Superior Técnico, ICEMS, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

^c Belarusian State University, Leningradskaya Str., 14, 220030 Minsk, Belarus

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ABSTRACT

New sodium and chloride ion-selective membrane cocktails for glass-capillary microelectrodes were developed satisfying the demands for corrosion studies. Membrane cocktails were optimized to provide a wide pH working range, good long-term stability and reproducibility of potential. The proposed sodium-selective cocktail contains sodium ionophore VI, potassium tetrakis(4-chlorophenyl) borate and 2-nitrophenyl octyl ether. The chloride-selective cocktail consists of tridodecylmethylammonium chloride and 2-nitrophenyl octyl ether. The proposed microelectrodes were successfully applied to measure the concentration of Cl^- and Na^+ over corroding cut-edge samples of metallic coated steel and can be recommended for measuring the distribution of Na^+ and Cl^- in corrosion applications.

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1. Introduction

Ions in the supporting electrolyte, or corrosion medium, Na^+ and especially Cl^- play an important role in several types of corrosion. It is commonly thought that, to maintain electroneutrality, Cl^- fluxes to the anodic reaction zones where formation of Me^{n+} is accompanied by local acidification of the medium due to the hydrolysis. Na^+ fluxes to the zone of supporting cathodic reaction where formation of OH^- ions takes place, promoting the corrosion process. Hence, monitoring the evolution of local concentrations of Cl^- and Na^+ together with pH and pM^{n+} measurements is of crucial importance for interpreting and modeling corrosion processes. Scanning ion-selective electrode technique using glass-capillary microelectrodes with liquid ion-selective membranes allows for obtaining direct information on local activities of the corresponding ions in a corrosion site. It therefore seems to be the most simple, convenient and informative method for this purpose.

Potentiometric measurements with glass-capillary microelectrodes, in their present form, have been widely used by physiologists for extra- and intracellular measurements since the early 1970s [1]. Such electrodes are advantageous, essentially because of their low cost and uniform manufacturing technology. The electrode consists

of a microcapillary with a tip diameter of 0.1–5 μm filled with an ion-selective membrane cocktail in its lower part. An inner reference solution (usually aqueous KCl solution) is placed above the membrane with a silver wire, coated by electrodeposited silver chloride, immersed into it. The analytical properties of such electrodes are determined by the composition of the liquid membrane. This usually consists of an organic solvent immiscible with water (e.g. 2-nitrophenyl octyl ether), a liquid anion- or cation-exchanger providing so-called perm-selectivity of the membrane to anions or cations respectively (e.g. tridodecylmethylammonium chloride and potassium tetrakis(4-chlorophenyl) borate), and an ionophore (e.g. valinomycin) providing the selectivity of the membrane to the ion of interest. While there is no problem to prepare any membrane cocktail from individual components in the laboratory, those more in demand are also commercially available.

The successful examples of application of glass-capillary microelectrodes in corrosion studies for pH [2–14], Zn^{2+} [15,16] and Mg^{2+} [6,8,14] activity mapping have been described. However, very few experimental results describe the Cl^- distribution in sites of pitting, crevice or cut-edge corrosion. Nguyen and Lin [17] used a double barrel chloride ion-selective microelectrode to follow the changes in Cl^- activity at the artificially delaminated area on the coating/metal interface and in a blister. They found that in both monitored sites of cold rolled steel, coated with an alkyd-based paint layer, Cl^- activity increased with immersion time. Luo et al.

* Corresponding author.

E-mail address: egorvv@bsu.by (V.V. Egorov).

Table 1
Cocktail compositions for sodium and chloride ISMEs.

# n/n	Ionophore		Ion exchanger		Solvent, up to 100 w/w %
	Name	w/w, %	Name	w/w, %	
1 ^a	Na ⁺ -ionophore II	10.0	Sodium tetraphenylborate	0.5	NPhOE
2	Na ⁺ -ionophore VI	6.1	KTCIPhB	2.3	NPhOE
3	Na ⁺ -ionophore VIII	2.8	KTCIPhB	0.5	NPhOE
4	Na ⁺ -ionophore X	0.7	KTCIPhB	0.2	NPhOE
5	Na ⁺ -ionophore VI	6.0	KTCIPhB	2.1	DMNB
6 ^a	Cl ⁻ -ionophore I	5.0	–	–	NPhOE ^b
7	Cl ⁻ -ionophore II	1.0	TDDMACI	0.1	NPhOE
8	–	–	TDDMACI	10.0	NPhOE

^a Commercially available membrane cocktails from Fluka [24].

^b Cocktail also contains 4.0 w/w % 1-Decanol and 1.0 w/w % tetradodecylammonium tetrakis(4-chlorophenyl) borate.

[18] measured Cl⁻ profiles over corroding pits. Lin et al. [19] measured accumulation of Cl⁻ over the crevice and pitting corrosion sites of stainless steel 304. Yan et al. [20] reported on the construction of combined Ag/AgCl – Ir/IrOx microelectrode that was used to monitor the increase in pH and depletion of Cl⁻ activity on X70 pipeline steel under cathodic protection. Du et al. [21] applied chloride selective microelectrodes to monitor Cl⁻ concentration at steel/concrete interfaces.

Although accumulation of Na⁺ under a delaminated coating is reported in multiple sources no experimental results, reporting measured Na⁺ concentration could be found in the literature until recently. All the studies mentioned above present fragmentary information. No systematic studies were undertaken in the direction of measuring Cl⁻ and Na⁺ distribution in various sites of corroding materials due to a lack of reliable experimental protocols. Meanwhile, information concerning the distribution of ions from the corrosive environment around active sites may be vital for modeling corrosion processes and corrosion prediction. For example, while modeling galvanic coupling in aluminum alloys, Murer et al. [22] concluded that the obstacle for the application of numerical mass transport models was the lack of input data on the local dissolution rate of aluminum matrix as a function of the chemistry of the system, namely pH and Cl⁻ concentration. Recently Lamaka et al. [14] reported on simultaneous micro-potentiometric measurements of Na⁺ and Cl⁻ activities over an anodically polarized Pt wire. For these experiments a number of commercially available membrane cocktails, namely sodium ionophore II – Cocktail A (Fluka Ref. 71178) and slightly modified (to decrease the electric resistance of the membrane and response time) chloride ionophore I – Cocktail A (Fluka Ref. 99408) have been utilized. After [14] was published, our attention was drawn to a possible pH dependence of these commercially available membrane cocktails. Said cocktails were developed for biological applications, where pH hardly varies for more than one tenth of a pH unit. Therefore their pH sensitivity was never an issue.

It should be mentioned here that, to obtain reliable results, a number of special requirements to analytical characteristics of Na⁺ and Cl⁻-selective microelectrodes should be fulfilled. Firstly, as far as pH in the corrosion zone can vary greatly from about 2

in the anodic zone to about 12 in the cathodic zone, there are high demands on the working pH range of both Na⁺- and Cl⁻-selective microelectrodes. Secondly, to register the alteration in Na⁺ and Cl⁻ activity which may be quite small (about 0.1–0.3 pa units of Cl⁻ and even less for Na⁺) high measurement precision is required. So the electrode should therefore provide small long-term potential drift and high potential reproducibility. Thirdly, high selectivity of the Na⁺-selective microelectrode against Zn²⁺, Al³⁺ and Mg²⁺ cations is necessary to prevent misinterpretation of Na⁺ activity measurements in anodic sites while working with metal coated steels and alloys. Lastly, to obtain scans including about one thousand or more experimental points within an appropriate timescale low response time of the used electrode is needed as well.

However, it turned out that Na⁺ and Cl⁻-selective microelectrodes based on the commercially available membrane cocktails do not fully satisfy the requirements mentioned above. So the aim of this work was to optimize the Na⁺ and Cl⁻-SME membrane composition by varying ionophore and solvent nature in order to achieve the required analytical characteristics for the microelectrodes. Both newly developed glass-capillary microelectrodes were applied to trace the changes of Na⁺ and Cl⁻ concentration over a cut-edge of Al-Zn coated steel.

2. Experimental

2.1. Equipment

Commercial Scanning Ion-selective Electrode Technique (SIET) equipment manufactured by Applicable Electronics (USA) and controlled using ASET software (ScienceWares, USA) with homemade glass capillary ion-selective electrodes (ISMEs) was used for performing the majority of the potentiometric measurements. ISMEs were made of single-barrel, standard-wall (330 μm), borosilicate glass capillaries with an outer diameter of 1.5 mm. A P-97 Flaming/Brown Micropipette Puller (Sutter Instruments Company) was used to shape the cone tip. The diameter of the orifice of the tip was 1.5 ± 0.3 μm. The capillaries were silanized by injecting 200 μl of N, N-dimethyltrimethylsilylamine in a glass preparation

Table 2
The membrane compositions for sodium and chloride macro electrodes.

# n/n	Ionophore		Ion exchanger		PVC, w/w %	Plasticizer, up to 100 w/w %
	Name	w/w, %	Name	w/w, %		
1	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	NPhOE
2	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	NPhPE
3	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	NPhPhE
4	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	DMNB
5	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	FPhNPhE
6	Na ⁺ -ionophore VI	1.0	KTCIPhB	0.4	33	BNPhE

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