ELECTROCHEMICAL ACTIVITY OF Fe(II) IONS IMMOBILIZED IN NAFION FILM ON GLASSY CARBON

S. Domagała[1]*, P. Krzyczmonik*[1]*, J. Dziegieć*[1]*, H. Scholl*[1]*, M. Cichomski*[2]*, J. Grobelny*[2]

[1] *University of Łódź, Department of General and Inorganic Chemistry, 90-136 Łódź, Poland*
[2] *University of Łódź, Department of Chemical Technology and Environmental Protection, 90-236 Łódź, Poland.*

Introduction

The proton polymer electrolytes have attracted much attention in recent years. They can be used in fundamental electrochemical investigations as chemical sensors, energy-producing or electrochromic devices. The chemically modified electrodes can serve as a powerful tool for investigation of electrocatalytical properties. Some metal ions after immobilization in a polymer film on electrodes conducting phase can act as redox mediators for anodic oxidation of organic compounds. Fe(III)/Fe(II) redox system is such effective mediator for the oxidation of some phenol, hydroquinone and aniline derivatives [1-7].
The aim of this work was to investigate the properties of glassy carbon modified with Fe(II) ions immobilized in Nafion film.

Experimental

The cyclic voltammetry measurements were done under an Ar atmosphere on potentiostat AUTOLAB (Eco Chemie BV) and the impedance measurements on potentiostat PAR 273A and the analyser of frequency SOLARTRON 1255, all in three electrode system, where the working and modified electrode was glassy carbon (GC), ϕ=1.5 mm, the reference electrode was saturated calomel electrode (SCE), and the counter electrode was the cylindric platinum gauze. The topography of the surface and phase images were obtained with the use of AFM, Solver P47 – NT-MDT [8,9]. A rectangular silicon cantilever (MicroMasch - product) consisting of pyramidal tip with radius *c.a.* 20 nm, stiffness *c.a.* 40 N/m and resonant frequency 170 kHz was used to scan the surface and to detect the phase signal. All measurements were done in a resonant mode.

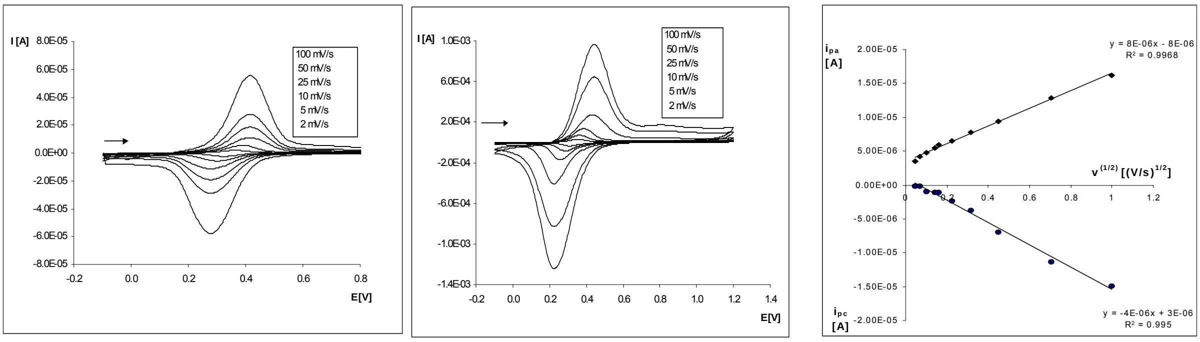
Results and discussion

In order to determine the properties of glassy carbon modified with Fe(II) ions immobilized in Nafion film the cyclic voltammetry and impedance measurements in three electrode system were done, where the working electrode was glassy carbon (GC) or modified glassy carbon (GC/Nafion/Fe(II)), the reference electrode was saturated calomel electrode (SCE), and the counter electrode was the cylindric platinum gauze. Figures 1a and 1b

---

Corresponding author: Sławomir Domagała
E-mail: domagala@chemul.uni.lodz.p)
Phone (+48 42) 635 57 76

show typical voltammetry plots of Fe(III)/Fe(II) redox system in 0.1 *M* $HClO_4$ solution on bare glassy carbon - GC (1a) and on glassy carbon modified with Fe(II) immobilized in Nafion - GC/Nafion/Fe(II) (fig.1b).



a) **b**) **c**)

Fig. 1 *The cyclic voltammograms **a**) of 0.01 M* $Fe(ClO_4)_2$ *in 0.1 M* $HClO_4$ *solution on bare GC, v=2-100 mV/s; **b**) of Fe(III)/Fe(II) redox couple on GC/Nafion/Fe(II) v=2-100 mV/s. **c**) Dependence of* $i_{pc}=f(v^{1/2})$ *for Fe(III)/Fe(II) system at GC/Nafion/Fe(II); v=2-100 mV/s.*

The voltammogram gave a steady state form on GC/Nafion/Fe(II) even after the repeated potential scanning which proves that the Fe(II) ions are effectively immobilized in Nafion film coated on glassy carbon.

The linear dependence of of the cathodic current (i_{pc}) on the square root of scan rate ($v^{1/2}$) shows that within the scan rate range 10-100 mV/s the redox process as well as in the solution and in the film is diffusion limited (fig. 1c).

The diffusion coefficients were calculated according to the equation $i_p=(2.69x10^5)n^{3/2} AC_0v^{1/2}D^{1/2}$ (25 °C).

Table 1 *The electrochemical data for Fe(III)/Fe(II) redox systems obtained from cyclic voltammetry, amperometric and coulometric measurements at glassy carbon.*

medium	redox system	$D_{app\ a}$ $[cm^2 s^{-1}]$	$D_{app\ c}$ $[cm^2 s^{-1}]$	α	β	k_{sa} $[cm\ s^{-1}]$	k_{sc} $[cm\ s^{-1}]$
solution	Fe(III)/Fe(II)	6.1×10^{-6}	6.7×0^{-6}	0.56	0.59	6.9×10^{-6}	5.4×10^{-6}
Nafion	Fe(III)/Fe(II)	9.2×10^{-7}	9.8×10^{-7}	0.53	0.52	6.3×10^{-7}	7.5×10^{-7}

The close values of both coefficients D_{app} in solution and in Nafion film can evidence that the global rate of transfer in the film is only one order of magnitude lower than in the solution. It suggests that Fe(III) ions are appropriate cations for the membrane model investigations.

In order to determine the changes of Fe(II) ions amount immobilized in Nafion film coated on GC (Γ), the 20 voltammetric cycles were done in each case, on GC/Nafion/Fe(II) in the scan rate range 10-100 mV/s in 0.1 *M* $HClO_4$ and then it was calculated from Γ=Q/nFA, where Q- is the charge [C], A- area of the conducting phase [cm^2], F- Faraday's constant, and n- number of electrons. The amount of Fe(II) ions immobilized in Nafion film has not been changed significantly after repeated scanning.

The impedance measurements (Fig. 2) show that the reaction of Fe(II) ions oxidation to Fe(III) within Nafion film is diffusion controlled process.

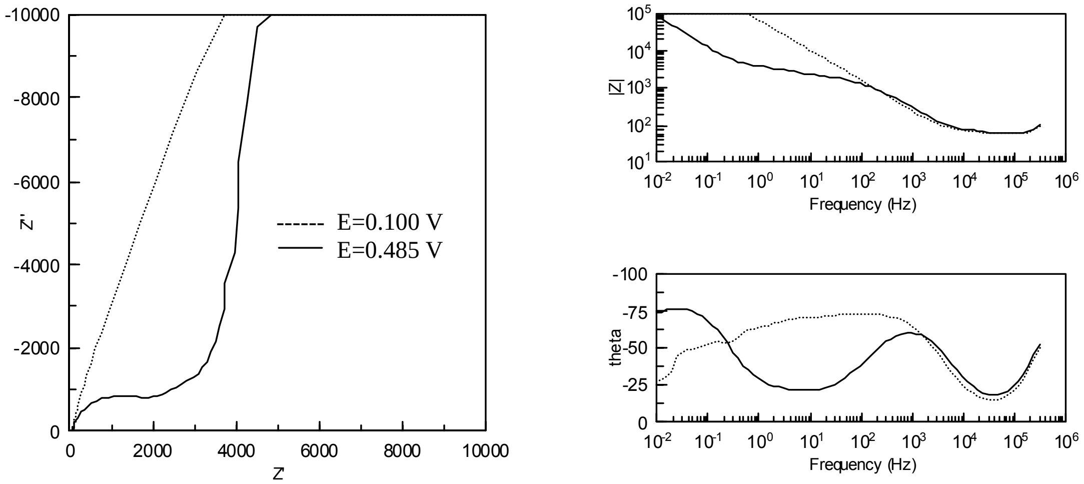


Fig. 2 The Nyquist's and Bode's diagrams for Fe(III)/Fe(II) system immobilized in Nafion film on glassy carbon (GC/Nafion/Fe(II)) at E=0.10 V and 0.485 V, amplitude 0.010 V, frequency range 3×10^{-5} *–* 1×10^{-2} *Hz.*

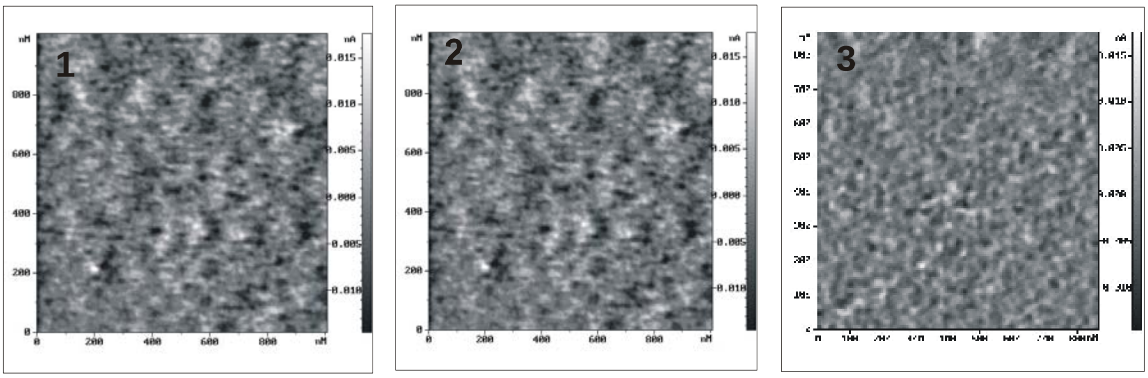


Fig. 3 *AFM pictures of: 1) glassy carbon; 2) Nafion layers on glassy carbon; 3) Nafion layers with immobilized Fe(II) ions on glassy carbon;*

Conclusions

The oxidation processes in the Fe(III)/Fe(II) redox couple immobilized in Nafion film on glassy carbon are the diffusion controlled processes. The small difference (about a magnitude of order) in values of diffusion coefficients D_{app} in solution and in Nafion film may suggest that Fe(III) ions are appropriate cations for the membrane model investigations. The AFM measurements (Fig. 3) show the cluster structure of polymer coatings. The mean value of the cluster size is 45 nm.

Acknowledgements

This work was financially supported by University of Łódź Grant nr 505/670 2004/2005.

References

1. R.W. Murray: Chemically Modified Electrodes, Electroanalytical Chemistry, Vol. 13, A.J. Bard, ed., Marcel Dekker Inc., NY, (1984).
2. R.P. Buck: Theory and Principles of Membrane Electrodes, Chapt. 1, Ion - Selective Electrodes in Analytical Chemistry, Vol. 1, H. Freiser, ed., Plenum Press, NY, (1978).
3. J.W. Ross, J.H. Riseman, J.A. Krueger: Pure Appl. Chem. **36** (4) (1973) 473.
4. L.C. Clark: Trans. Am. Soc. Artif. Int. Organs. **2** (1956) 41.
5. L.H. Dubois, R.G. Muzzo: Anal. Rev. Phys. Chem. **43** (1992) 437.
6. J.Langmaier, A. Trojanek, J.Weber, Z.Samec: J.Electroanal. Chem. **469** (1999) 11.
7. J.Dziegieć, S.Domagała: Annals of the Polish Chemical Society **2** (2003) 1015.
8. G. Binning, C.F. Quate, C. Gerber: Phys. Rev. Lett. **56** (1986) 530.
9. B. Raton: Modern Tribology Handbook CRC Press FL, Vols. I, II (2001).