

ELECTROCHEMICAL ACTIVITY OF Ce(III) IONS IMMOBILIZED IN NAFION FILM ON PLATINUM

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Introduction

The proton polymer electrolytes can be used in fundamental electrochemical investigations as chemical sensors, energy-producing, electrochromic devices or as a membrane in fuel cells. 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. Ce(IV)/Ce(III) redox system is such effective mediator for the oxidation of some organic compounds and charge mediator within polymer film [1-7].

The aim of this work was to investigate the properties of platinum modified with Ce(III) ions immobilized in Nafion film.

Experimental

The cyclic voltammetry measurements were done under an Ar atmosphere on potentiostat AUTOLAB (Eco Chemie BV), the impedance measurements were performed on potentiostat PAR 273A and the analyser of frequency SOLARTRON 1255. All experiments were done in three electrode system, where the working and modified electrode was platinum (Pt), $\phi=1.5$ mm, the reference 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 platinum modified with Ce(III) ions immobilized in Nafion film the cyclic voltammetry and impedance measurements in three electrode system were carried on platinum (Pt) or modified platinum (Pt/Nafion/Ce(III)). Figures 1a and 1b show typical voltammetry plots of Ce(IV)/Ce(III) redox system in 0.1M HClO₄ solution on bare platinum - Pt (1a) and on platinum modified with Ce(III) immobilized in Nafion - Pt/Nafion/Ce(III) (fig.1b).

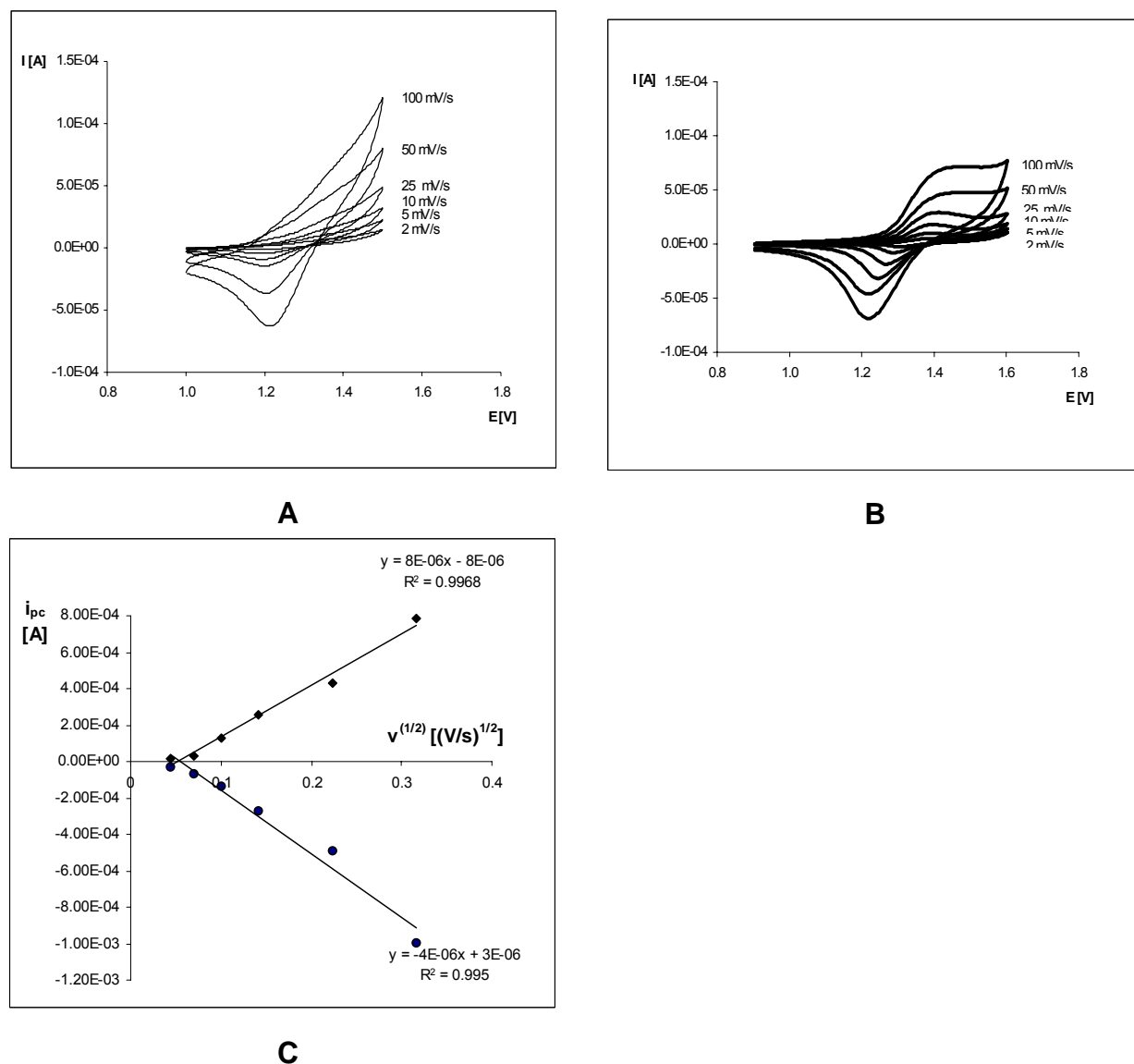


Fig. 1 The cyclic voltammograms A) of 0.01 M Ce(ClO₄)₃ in 0.1 M HClO₄ solution on bare Pt, $v=2$ -100 mV/s; B) of Ce(IV)/Ce(III) redox couple on Pt/Nafion/Ce(III) $v=2$ -100 mV/s. C) Dependence of $i_{pc}=f(v^{1/2})$ for Ce(IV)/Ce(III) system at Pt/Nafion/Ce(III); $v=2$ -100 mV/s.

The voltammogram gave a steady state form on Pt/Nafion/Ce(III) even after the repeated potential scanning which proves that the Ce(III) ions are effectively immobilized in Nafion film coated on platinum.

The linear dependence 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 $i_p = (2.69 \times 10^5) n^{3/2} A C_0 v^{1/2} D^{1/2}$ (25 °C).

Table 1 The electrochemical data for Ce(IV)/Ce(III) redox system obtained from cyclic voltammetry, amperometric and coulometric measurements at platinum.

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	Ce(IV)/Ce(III)	1.1×10^{-5}	1.2×10^{-6}	0.53	0.54	4.6×10^{-6}	4.4×10^{-6}
nafion	Ce(IV)/Ce(III)	1.9×10^{-7}	1.6×10^{-7}	0.51	0.52	5.3×10^{-7}	5.7×10^{-7}

In order to determine the changes of Ce(III) ions amount immobilized in Nafion film coated on Pt (Γ), the 20 voltammetric cycles were done in each case, on Pt/Nafion/Ce(III) in the scan rate range 10-100 mV/s in 0.1 M HClO₄ and then it was calculated from $\Gamma = Q/nFA$, where Q - is the charge [C], A - area of the electrode [cm²], F - Faraday's constant, and n - number of electrons. The amount of Ce(III) ions immobilized in Nafion film did not change significantly after repeated scanning.

The impedance measurements (Fig. 2) show that the oxidation of Ce(III) to Ce(IV) within Nafion film is diffusion controlled process.

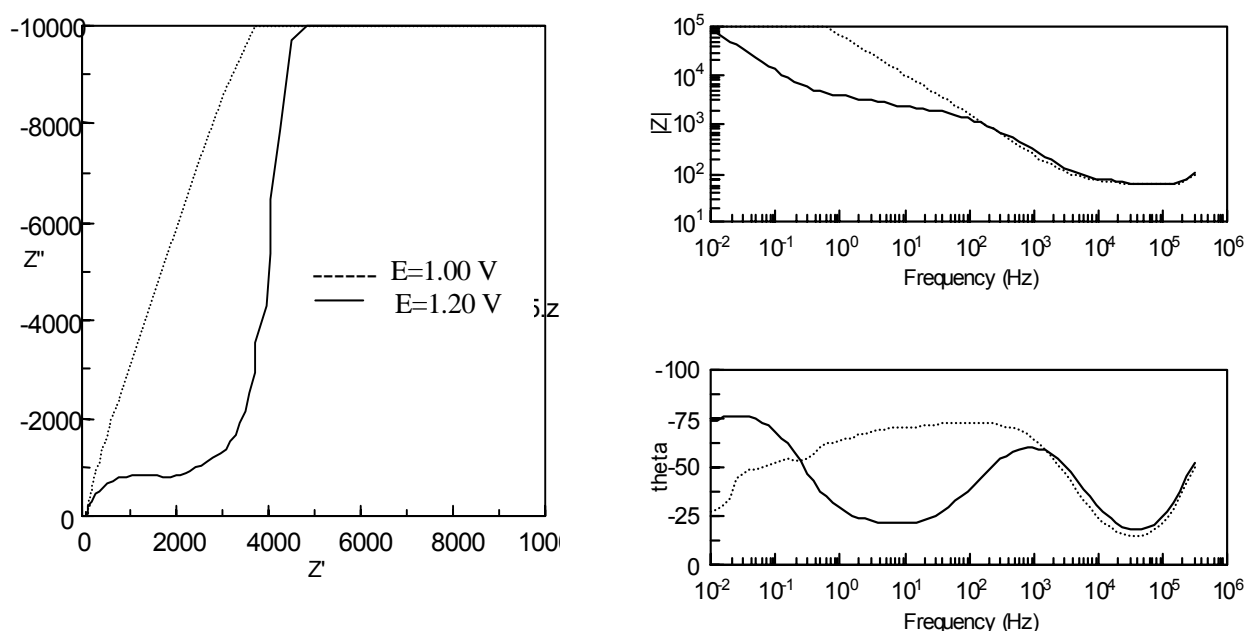


Fig. 2 The Nyquist's and Bode's diagrams for Ce(IV)/Ce(III) system immobilized in Nafion film on platinum (Pt/Nafion/Ce(III)) at $E=1.10$ V and 1.234 V, amplitude 0.010 V, frequency range $3 \times 10^{-5} - 1 \times 10^{-2}$ Hz.

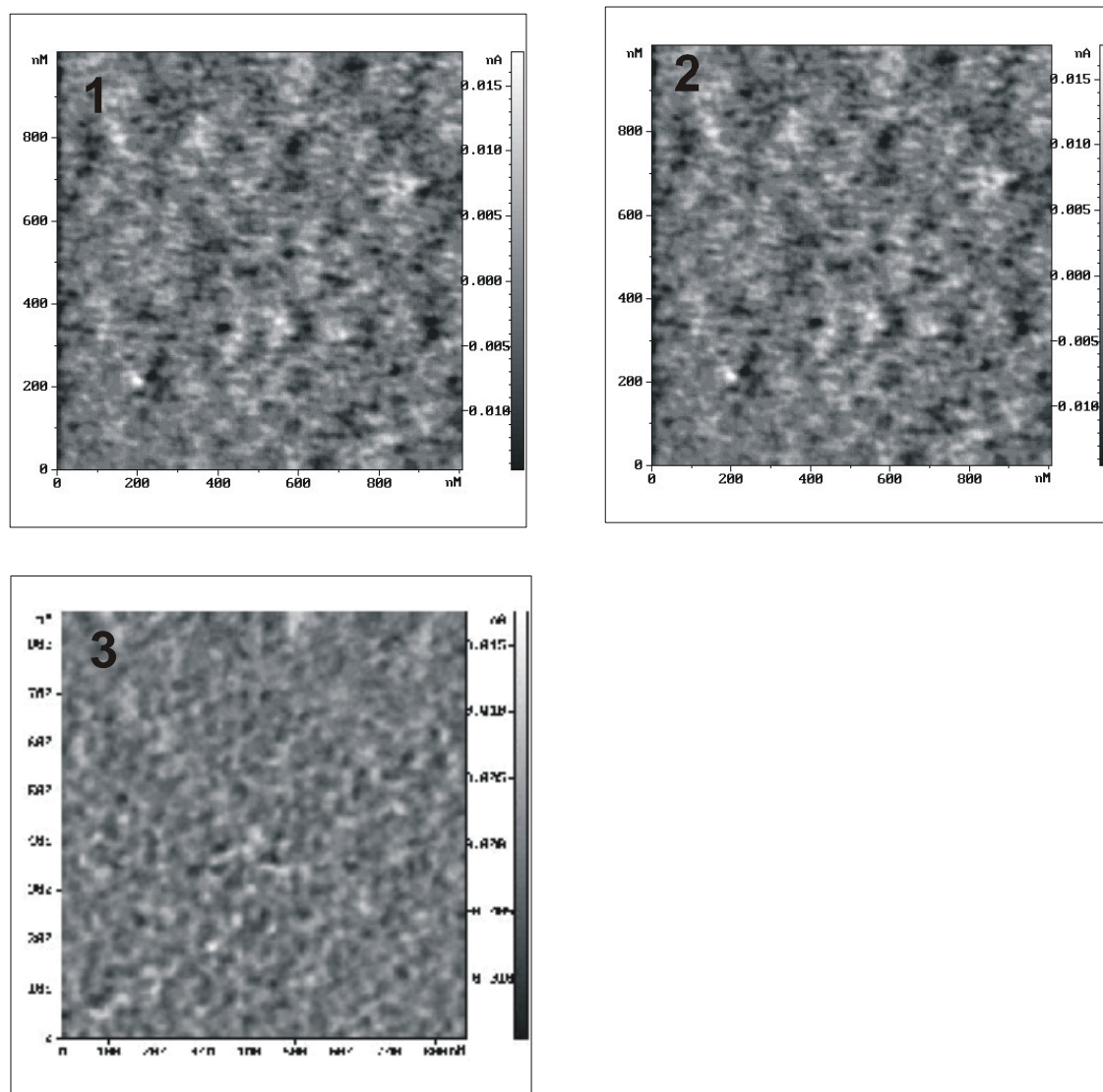


Fig. 3. . AFM pictures of: 1) platinum; 2) Nafion layers on platinum; 3) Nafion layers with immobilized Ce(III) ions on platinum.

Conclusions

The oxidation processes in the Ce(IV)/Ce(III) redox couple immobilized in Nafion film on platinum are the diffusion controlled processes. The fast charge transfer within Nafion film may suggest that Ce(IV)/Ce(III) redox couple is appropriate for the membrane model investigations as well as for charge mediator in fuel cell membrane. The AFM measurements (Fig. 3) show the cluster structure of polymer coatings. The mean value of the cluster size is ca. 41 nm.

Acknowledgements

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