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Conference Paper**Oxygen Reduction in Aqueous Phosphate Solutions. Properties of Fe, Co, Ni, Cu Impregnated Polyphthalocyanines****M. Savy, P. Andro, and C. Bernard**Laboratoire d'Electrolyse du C. N. R. S., 92-Bellevue, France*

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The oxygen reduction process has been investigated at room temperature on polyphthalocyanines of Fe, Co, Ni and Cu prepared similarly impregnated in acetylene black on a graphite support. Fe polyphthalocyanine is the most active. Investigations *versus* pH and temperature have shown that the limiting process is a 4 electron transfer.

INTRODUCTION

Data have been already published by several authors^{1,2} concerning monomer and polymer phthalocyanine properties with respect to oxygen reduction.

The activity of the Fe phthalocyanine polymer in acidic medium has been demonstrated for the first time by Janke. Unfortunately the type of electrode, which was used, was not suitable for reaction mechanism determination.

On monomeric systems, we have been able to propose a model of oxygen reduction processes which is compatible with our data. Its main characteristic³ is an attempt to correlate the catalytic activity observed with the electronic properties of FePc monomer as determined by solid state investigations.

The data published at the 21st C.I.T.C.E. meeting are presented on Fig. 1.

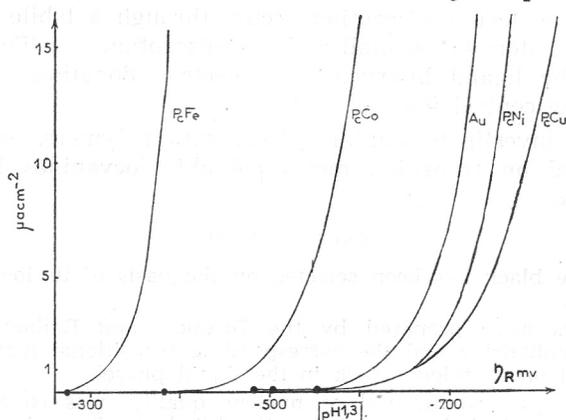


Fig. 1. Current-voltage characteristic for oxygen reduction on Cu, Ni, Co and Fe phthalocyanine monomers.

* Based on a lecture presented at the 22nd Meeting of the International Society of Electrochemistry, Dubrovnik, Yugoslavia, September 1971.

In the acid and neutral media investigated under the same crystalline form, the FePc monomer is the most active. Fe and CoPc are independent of the pH, more active than the gold support.

On Fig. 2 a possible mechanism for oxygen reduction on phthalocyanine monomer is presented. The specific activity of Fe phthalocyanine is interpreted

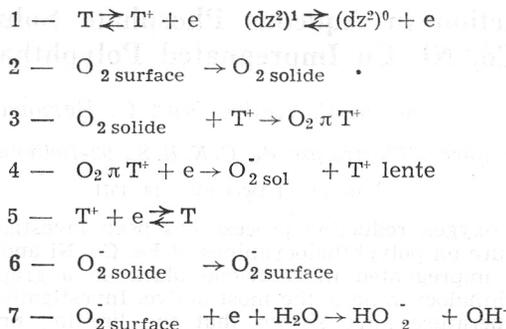


Fig. 2. Oxygen reduction processes mechanism on phthalocyanine monomers.

as being due to the ability to chemisorb oxygen. Several criteria have to be satisfied from considerations of the theories of catalysis. They are mainly connected with free enthalpy change, and electronic distribution in the energy levels of the adsorption site and in the adsorbed oxygen molecule⁴. The maximum activity for electronic exchange is realized when a half filled electronic level of the oxygen molecule is located close in distance and energy to a half filled corresponding level of the adsorption site.

The distinguish in characteristic of FePc which differentiates it from the other Pc compounds is the existence of two forms high and low spin at room temperature⁵.

The oxygen molecule adsorption occurs through a labile π bonding between one oxygen atom (π^* orbital) and the adsorption site (Fe^{II} atom dxz and dyz orbitals). The ligand intervenes by electron donation or acceptance (π bonding with the central ion).

In order to investigate similar effects with polymers, oxygen reduction has been studied on transition metal polyphthalocyanines impregnated on acetylene blacks.

EXPERIMENTAL

The acetylene black has been selected on the basis of its low activity toward oxygen reduction.

The polymers were prepared by the Drunkar and Bailar⁶ technique from the pyromellitic anhydride and the corresponding transitional metal chlorides and were impregnated on acetylene black in the liquid phase⁷.

The electrode, a graphite rod of nuclear quality, was covered with a thin deposit of acetylene black impregnated with phthalocyanine polymer. The catalyst deposition was performed by several methods.

Mixtures of impregnated acetylene black were formed and heated to volatilize unstable components on the electrode and then furtherly baked under vacuum at 10^{-4} torr.

The electrochemical activity has been investigated by the classical tensiocinetic technique in a range of pH from 1.3 to 13, 0.2 Molar in phosphate ions. A voltage sweep rate of 0.16 mV.s⁻¹ has been selected in order to obtain a quasi steady current density.

The data obtained at pH 1.3 for Cu, Ni, Co and Fe phthalocyanine polymers are represented on Fig. 3. Table I is a comparison of the polymers with the monomers at the same pH, on gold support.

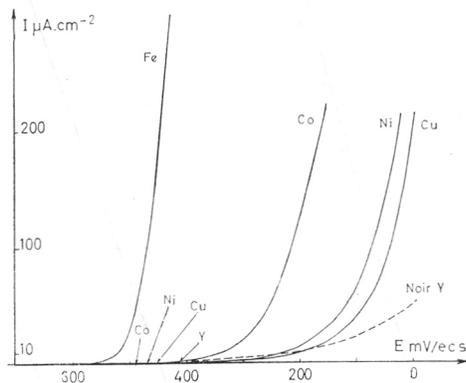


Fig. 3. Current-voltage characteristic for oxygen reduction on Cu, Ni, Co and Fe polyphthalocyanine polymers at pH 1.3.

TABLE I

Comparison of Monomers with Polymers

pH 1.3	Polymers				Monomers			
	Cu	Ni	Co	Fe	Cu	Ni	Co	Fe
Rest potentials SCE	450	470	490	580	400	420	540	630
Slope mv/deca.			100	45	100	85	65	55

At pH 6.7 polymers for Fe and Co data are represented by Fig. 4. The order of activity Fe > Co > Ni ≥ Cu remains the same both for the polymer and monomer forms independent of the pH. The rest potential and the Tafel slope are higher for the iron monomers than for the polymers.

Fe polyphthalocyanine has been investigated in more details for a determination of the reaction mechanism. Data are represented as a function of pH on Fig. 5. The slopes and the rest potentials are given by Table II.

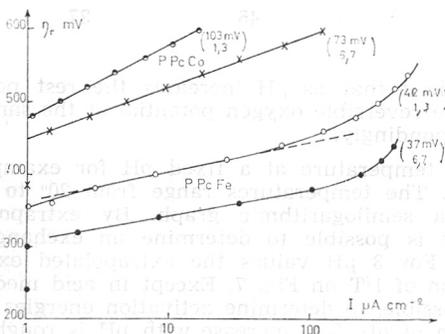


Fig. 4. Comparison of the activity of Co and Fe polyphthalocyanine at pH 1.3 and pH 6.7.

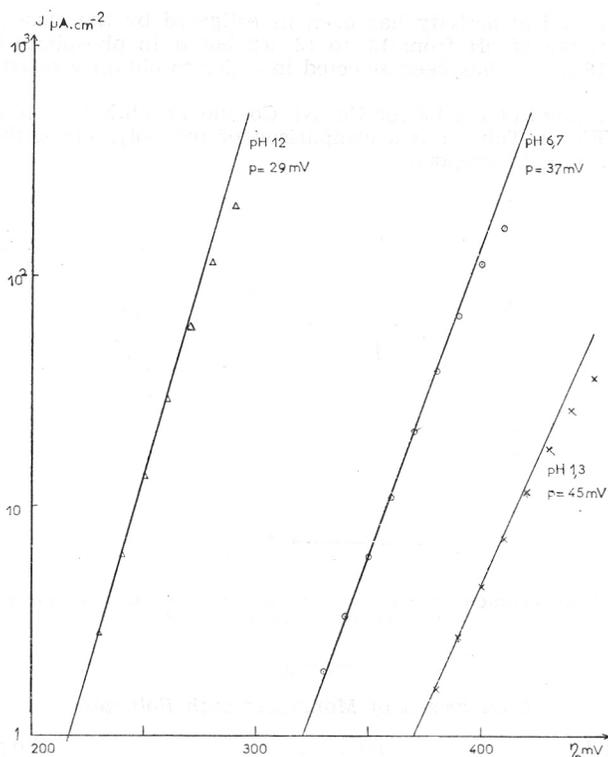


Fig. 5. Current voltage characteristic for oxygen reduction on Fe polyphthalocyanine at different pH.

TABLE II

Shape and Rest Potential on Fe Polyphthalocyanine

pH	1.3	6.7	12
Zéro current SCE potential (mV)	580	320	55
slope mV/decade	45	37	29

It should be noticed that as pH increases the rest potential becomes more anodic compared to the reversible oxygen potential at the same pH, while the Tafel slope decreases correspondingly.

As a function of temperature at a fixed pH for example 6.7, the activity is represented on Fig. 6. The temperatures range from 20° to 80° C. Current-voltage plots are linear in a semilogarithmic graph. By extrapolation to the oxygen reversible potential it is possible to determine an exchange current at a given temperature and pH. For 3 pH values the extrapolated exchange current is represented as a function of $1/T$ on Fig. 7. Except in acid medium straight lines are obtained. It is thus possible, to determine activation energies which are represented in Fig. 8 as a function of pH. The increase with pH is roughly linear with a slope of $4.6 RT$ per pH unit.

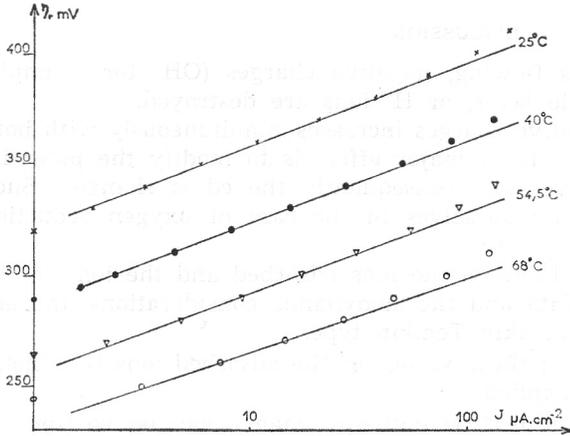


Fig. 6. Current-voltage characteristic for oxygen reduction on Fe polyphthalocyanine at different temperatures.

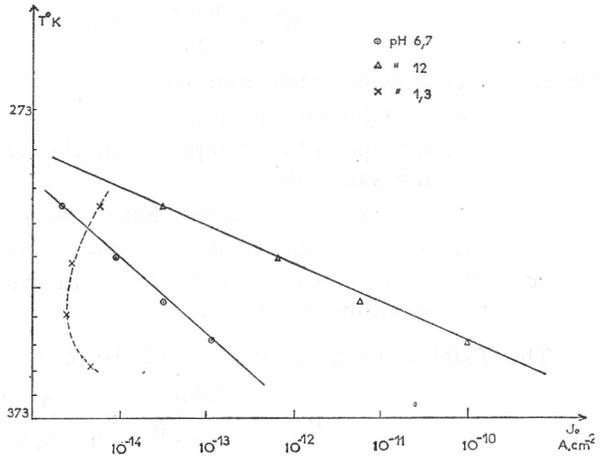


Fig. 7. Plots versus $1/T$ of the extrapolated exchange current densities for different pH.

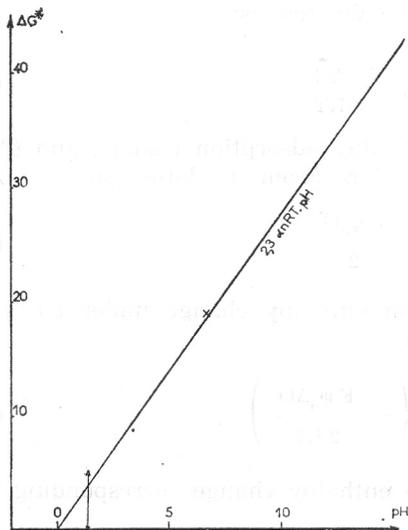


Fig. 8. Plots of the activation energy versus pH.

DISCUSSION

When cathodic current is flowing, negative charges (OH^- for example) are introduced into the double layer, or H^+ ions are destroyed.

This accumulation of negative charges increases simultaneously with both the overvoltage and with the pH. A major effect is to modify the potential distribution in the double layer and consequently the cd is changed. Such effect has been investigated by ourselves in the case of oxygen reduction on gold⁸.

Assuming an equilibrium between the ions adsorbed and the ions in the solution, from experimental data and thermodynamic considerations, the adsorption isotherm is of the Frumkin Temkin type.

In addition, the variation of the coverage of the adsorbed ions is a linear function of the overvoltage applied.

The electrochemical activation free enthalpy change can be written as:

$$\Delta \Delta G^* = \frac{n \alpha F}{2 \nu} [\eta - \eta_0 + \psi_0 \Delta \Theta] \quad (1)$$

- where
- ν : stoichiometric number,
 - α : transfer coefficient,
 - η_0 : rest potential compared to the oxygen reversible potential at the same pH,
 - n : number of electrons transferred,
 - $\Delta \Theta$: ion coverage variation from the rest potential,
 - Ψ_0 : constant equal to the potential drop in the double layer corresponding to $\Theta = 1$.

The Tafel slope as a function of $\Delta \Theta$ can be written as:

$$p = - \frac{1.6 RT \nu}{n \alpha F} \frac{\eta - \eta_0}{\eta - \eta_0 + \psi_0 \Delta \Theta} \quad (2)$$

In addition, the adsorption isotherm can be written as:

$$\frac{\Theta}{1 - \Theta} = (A^-) \exp - \frac{\Delta \tilde{G}^-}{RT} \quad (3)$$

where $\Delta \tilde{G}^-$ is the electrochemical free enthalpy adsorption change, and (A^-) is the activity of negative ions in the solution. From its definition:

$$\Delta \tilde{G}^- = \Delta G^- + \frac{F \psi_0 \Theta}{2} \quad (4)$$

where ΔG^- is the free chemical adsorption enthalpy change under current drain. (3) can be written assuming $\Theta \ll 1$

$$\Theta = (A^-) \exp \left(- \frac{\Delta \tilde{G}_0^-}{RT} \right) \exp \left(- \frac{F \psi_0 \Delta \Theta}{2 RT} \right) \quad (5)$$

$\Delta \tilde{G}_0^-$ is the theoretical electrochemical free enthalpy change corresponding to the reversible potential.

$\Delta\Theta$ theoretical coverage variation on the electrode between the applied potential and the reversible oxygen potential at a given pH.

For two pH values, assuming a relatively small change in the coverage value, it can be written:

$$\exp\left(\frac{F\psi_0[\Theta\Delta_1 - \Delta\Theta_2]}{2RT}\right) = \frac{(A_1^-)}{(A_2^-)} \exp\left(-\frac{\Delta\tilde{G}_{01} - \Delta\tilde{G}_{02}}{RT}\right) \quad (6)$$

where subscripts 1 and 2 refer to each pH value.

$\Delta\tilde{G}_{01}$ and $\Delta\tilde{G}_{02}$ are the theoretical free enthalpy changes at the corresponding pH.

Per pH unit one can obtain:

$$\frac{\Delta\Delta\Theta}{\Delta\text{pH}} = \frac{4.6RT}{F\psi_0} - \frac{2\Delta\Delta\tilde{G}_0}{F\psi_0} \quad (7)$$

expressing $\Delta\Theta$ as a function of pH. By substituting into equation (1):

$$\frac{\Delta\Delta\tilde{G}^*}{\Delta\text{pH}} = 4.6RT - \frac{2\Delta\Delta\tilde{G}_0}{\Delta\text{pH}} \quad (8)$$

Experimentally at 25°C, we find a variation of 2.7 kcal/Mol pH, which means substituting this value in equation (8):

$$\left(\frac{\Delta\Delta\tilde{G}_0}{\Delta\text{pH}}\right)_{\eta=0} \ll 2.3RT \quad (9)$$

CONCLUSION

As a conclusion, it can be pointed out that on Fe polyphthalocyanine properties concerning oxygen reduction processes differ strongly from the other polymers. The activity is greater than on the other polyphthalocyanines, the rest potential being more anodic while the Tafel slope independently of the pH is always lower. In addition, from investigations versus pH and temperature, it follows that the limiting factor is not the oxygen chemisorption but an electron transfer where $\nu = 1$. This yield a Tafel slope which varies continuously from 45 mV/decade at pH 1.3 to 29 mV/decade at pH 13. This change can be interpreted as being due to accumulation of negative charges in the electrical double layer. This effect enhances the catalytic process.

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IZVOD

Redukcija kisika u vodenim otopinama fosfata. Svojstva impregniranih Fe, Co, Ni i Cu-polifitalocijanina

M. Savy, P. Andro i C. Bernard

Ispitivana je redukcija kisika na polifitalocijaninima Fe, Co, Ni i Cu, koji su pripremljeni impregnacijom s acetilenskom čađom na grafitnom podlošku. Pronađeno je da je Fe-ftalocijanin kao Fe-polifitalocijanin najaktivniji. Kod $pH = 1,3$ potencijal mirovanja je najpozitivniji u seriji ispitivanih tvari, a nagib Tafelovog pravca najmanji (45 do 55 mV/log gustoće struje). Stupanj koji određuje brzinu reakcije nije komisorpcija kisika, nego prijenos elektrona sa stehiometrijskim brojem = 1.

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