

Characterisation of platinum electrode modified with phosphate rock for Cd²⁺ ions detection

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Abstract - *In the present paper we report the characterization of platinum electrode modified with a polymeric membrane. The use of natural minerals such as phosphate rock (PR) from the mine of Djebel Onk (Algeria) was investigated as ionophore for Cd²⁺ ions detection. The impedance data were adjusted from 100 mHz to 100 kHz and at polarisation - 200 mV. The maximum exchange was obtained between pH 4 and 6. Low detection limit is about 10⁻⁵ M.*

Résumé - *L'objectif de ce travail est la fonctionnalisation d'une électrode de platine modifiée par une membrane polymérique, en choisissant le phosphate naturel de Djebel Onk (Algérie) comme ionophore sensible aux ions Cd²⁺. La caractérisation a été étudiée par la spectroscopie d'impédance électrochimique à une polarisation de - 0,2 V / SCE et dans un domaine de fréquence qui varie de 100 kHz à 100mHz. L'échange de l'ion Cd²⁺ est maximum au pH 4 à 6. La limite de détection obtenue est 10⁻⁵ M.*

Keywords: Electrochemical sensors - Phosphate rock - Impedance spectroscopy - Ion exchange.

1. INTRODUCTION

An intensive development in the field of the development in the determination of chemical species in solution has been observed during the last two decades. This tendency is especially noticeable in environmental monitoring and industrial process control, which require continuous and on-site measurements [1, 2].

In fact, the presence of heavy metals in water supplies may cause adverse effects on the ecosystem and human health [3, 4]. In order to satisfy the need of chemical, industrial and environmental analyses, the interest in chemical sensors has increased sharply [5].

Ion sensitive sensors are composed of a sensitive part including a specific ionophore deposited on a transducer; several approaches can be used for the functionalization of these transducing surfaces [6]. Recently natural materials are used for this method and they have gained importance.

The abundance of natural phosphate, its low price and non-aggressive nature towards the environment are advantages for its utilisation in point of view of wastewater and wastes clean up [3]. Phosphate minerals, including hydroxyapatite, have also been demonstrated to effectively immobilize heavy metals such as Pb from aqueous solutions and metal contaminated soils [7, 8].

The possible mechanisms for metal retention by phosphate minerals included: ion-exchange processes at the surface of phosphate rock (PR) [9, 10]; surface complexation [10]; precipitation of some amorphous to poorly crystalline, mixed metal phosphates [11]; substitution of Ca in PR by other metals during recrystallisation [10, 12, 13].

The main objective of this study is to investigate the feasibility of using PR as ionophore in order to elaborate polymeric membrane sensitive to Cd^{2+} from aqueous solutions.

Plasticized polyvinyl chloride (PVC) is the most commonly used ionophore support [14-17]. A specific attention has been paid to the study phenomena occurring at the modified electrode/electrolyte.

Electrochemical impedance spectroscopy allows to characterise both resistive and capacitive proprieties of materials based on perturbation of a systems at equilibrium by a sinusoidal excitation signal of small amplitude, the measurement are carried out at different frequencies analyses of the system response contains informations concerning the interface [6, 18].

2. MATERIALS AND METHODS

2.1 Materials

The mineral phosphate rock used in this study was from the mine of Djebel Onk (East of Algeria). It was washed with distilled water and dried at 103 °C for 24 h to remove moisture. The fraction between 100 and 400 μm grain size which contain phosphate phases was retained and ground to obtain a homogenous sample having a grain size below 125 μm .

The chemical composition of PR is given in **Table 1**. The mineralogical composition of the PR was presented in Bezzi *et al.* [18]. Fluoroapatite carbonated was identified as a major component of this PR. Dolomite, calcite and quartz are the other associated gangue minerals.

Table 1: Chemical composition of PR sample

Analysis	Results (%)
P_2O_5	29.04
CaO	49.89
MgO	1.15
CO_2	7.18
SiO_2	2.14
Fe_2O_3	0.31
Al_2O_3	0.39
SO_3	3.22
K_2O	0.15
Na_2O	1.21
F	3.68
Cl	0.04
Organic matter	0.26
Moisture	0.76

2.2 Composition and deposition of the membrane

For the preparation of Cd(II)-membranes, typical procedure was applied using phosphate rock ionophore, polyvinylchloride (PVC) and dioctylphthalate (plastizer) in a ratio 10 %, 20 %, 70 % respectively; diluted in 1ml tetrahydrofuranne (THF); 5 μ l of polymeric membrane was deposited on platinum electrode, The solvent being then evaporated at ambient air.

The sensor was then soaked for $\frac{1}{2}$ h in 10^{-1} M CdCl₂ solution to achieve appropriate conditioning of the PVC/ionophore membrane. The electrolyte chosen for these measurements was KNO₃ 10^{-1} M with pH \approx 6.7.

2.3 Impedance measurements

The measurement set-up used an electrochemical cell with three electrodes: auxiliary platinum electrode, saturated calomel electrode (SCE) and the modified platinum electrode ($\phi = 0.5$ mm) as working electrode. The impedance analysis was performed with a voltalab 40 (radiometer analytical,SA) and PGZ301 as a potentiostat, software volta master 4 was used for the acquisition of the data and the control of the experiments.

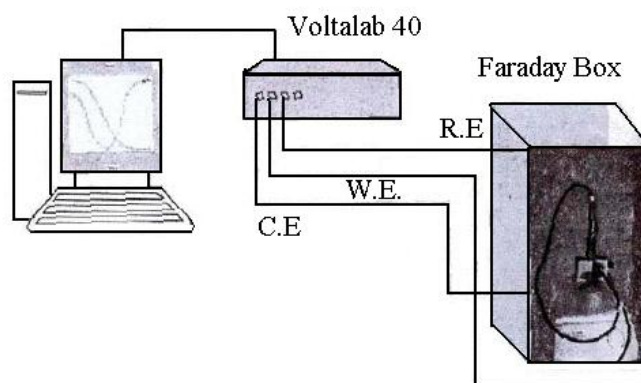


Fig. 1: Experimental set up to carry out impedance measurements

All the data were obtained with a 10 mV modulation voltage and a frequency range varying from 100 kHz to 100 mHz. Solutions for testing the ion-sensitivity were CdCl₂ in the concentration range of 10^{-7} to 10^{-4} M in 0.1 M KNO₃, pH \approx 6.7. The experiments were performed in a dark and grounded metal box to eliminate electrical interferences.

3. RESULTS AND DISCUSSION

3.1 Optimisation of experimental conditions

In the first time, experimental conditions were optimized in terms of voltage and frequency; for a polarisation -0.2V/SCE. The impedance measurements realized before and after the membrane deposition presented in the complex plane are shown in Fig 2.

We can see that at high frequencies the impedance is not modified however, at low frequency, the impedance of the electrochemical system decreases; this renders possible the observation of the ion exchange sensitivity influence especially at low frequency.

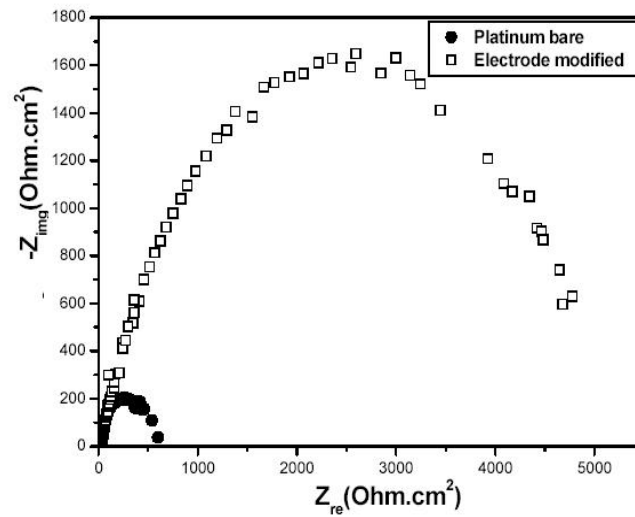


Fig. 2: Nyquist plot at polarisation -0.2 V, frequency: 100 kHz – 100 mHz

3.2 Impedance analysis of functionalized platinum electrode

In the presence of cadmium ions, we can (Fig. 3) that at high frequencies the impedance is not modified. However, at low frequency, the impedance of the electrochemical system decreases significantly with increasing concentrations of Cd^{2+} .

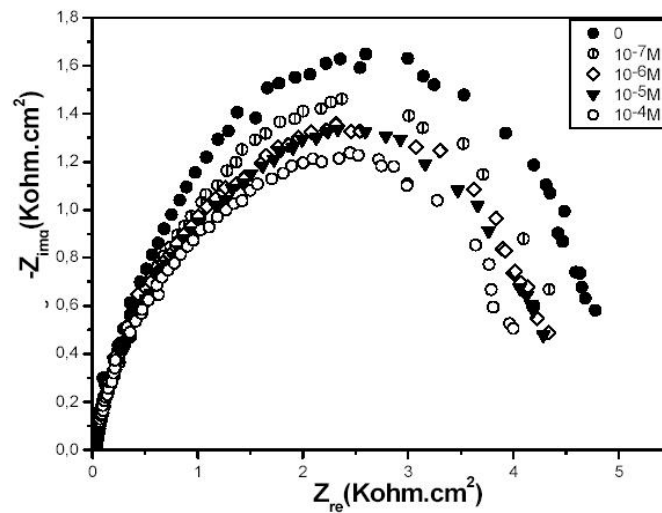


Fig. 3: Evolutions of Nyquist spectra v.s. concentrations of Cd(II) supporting electrolyte: 0.1M KNO_3 , $\text{pH} \approx 6.7$

In the Nyquist diagram, the approximate form is a semi-circle, characteristic of the association of a resistance in parallel with a capacity. It is important noteworthy that the semi-circular decreases when increasing concentrations of cadmium.

3.3 Influence of pH variation

The pH variation was obtained by additions of 1 M of HCl and NaOH solutions. We have chosen working interval of pH from 2.3 to 11 at 10^{-4} M of Cd^{2+} concentration. Fig. 5 shown the charge-transfer evolution function of pH. We can see that the PVC/PR membrane is sensitive in a relatively acid pH range 4 to 6.

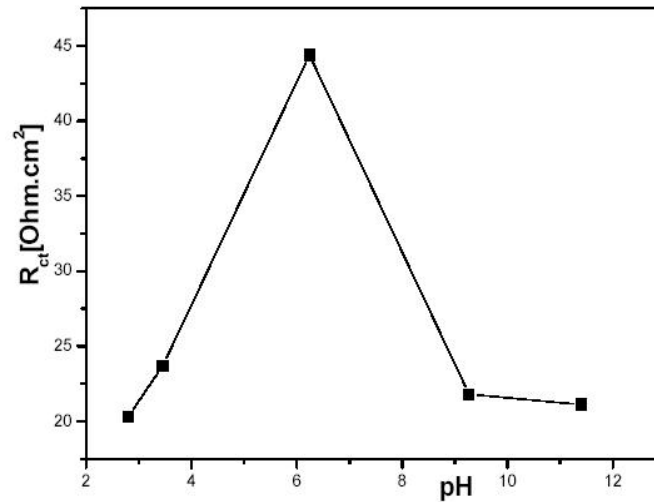


Fig. 4: Variation of charge transfer resistance as function of pH

3.4 Calibration curves

To obtain the calibration curve of Cd(II) -sensitive sensor, we have plotted the variations of R_{ct} versus Cd(II) concentrations. R_{ct} being the charge-transfer resistance of different concentrations of Cd(II) (Fig. 5).

From the obtained data, it is seen that the sensor presents dynamic range from 10^{-4} M to 10^{-5} M with a detection limit of about 10^{-5} M.

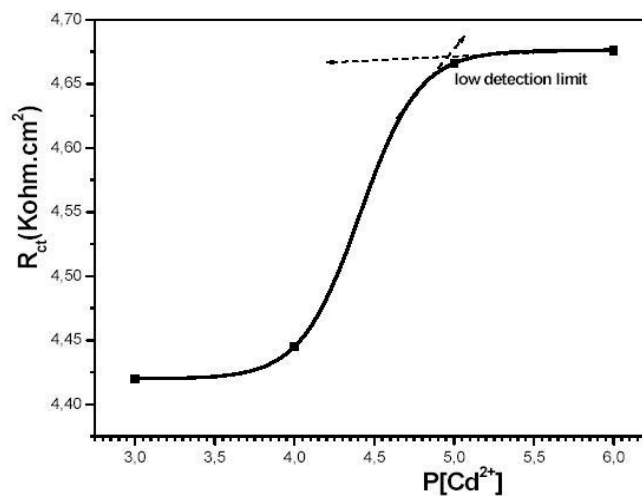


Fig. 5: Variation of the charge transfer resistance as function Cd(II) concentration

4. CONCLUSION

This study has been shown that a good electrochemical sensor for Cd²⁺ detection was obtained with phosphate rock as a natural ionophore which replace expensive synthetic compound. The maximum exchange was obtained between pH 4 and 6 and low detection limit is about 10⁻⁵ M.

This result can be obtained in specific conditions of measurements: frequency range varying from 100 mHz to 100 kHz and the polarisation was maintained at -0.2V/SCE. We suggest using similar membrane to functionalized ISFET sensor for Cd²⁺ detection.

REFERENCES

- [1] C. Cali, D. Fiox, G. Taillades, E. Siebert, D. Gonbeau, A. Pradel and M. Ribes, '*Copper (II) Selective Electrode Based on Chalcogenide Materials: Study of the Membrane/Solution Interface with Electrochemical Impedance Spectroscopy and X-ray Photoelectron Spectroscopy*', Materials Science and Engineering C, Vol. 21, pp. 3 – 8, 2002.
- [2] A.V. Legin, E.A Bychkov and Y.G. Vlasov, '*Analytical Applications of Chalcogenide Glass Chemical Sensors in Environmental Monitoring and Process Control*', Sensors and Actuators B: Chemical, Vol. 24, N°1-3, pp. 309 – 311, 1995.
- [3] A. Aklil, M. Mouflih and S. Sebti, '*Removal of Heavy Metal Ion from Water by Using Calcined Phosphate as New Adsorbent*', Journal of Hazardous Materials A, Vol. 112, pp. 183 – 190, 2004.
- [4] T. Skowronski, J. Pirszel and B. Pawlik-Skowronska, '*Heavy Metal Removal by Waste Biomass of Penicillium Chrysogenum*', Water Qual. Res. J. Canada, Vol. 36, N°4, pp. 793 – 803, 2001.
- [5] H. Barhoumi, A. Maaref, R. Mlika, C. Martelet, N. Jaffrezic-Renault and L. Ponsonnet, '*EIS Field Effect Structures Functionalized by P-Tert-Butylcalix[6]Arene for Ni²⁺ Detection*', Materials Science and Engineering C, Vol. 25, N°1, pp. 61 – 66, 2005.
- [6] M. Ben Ali, T. Homri, Y. Korpan, A. Abdelghani, M.A. Maaref, L. Liu, N. Jaffrezic-Renault and C. Martelet, '*Electrical Characterisation of Functionalized Platinum Electrodes and ISFET Sensors for Metal Ion Detection*', Materials Science and Engineering C, Vol. 26, N°1, pp. 149 – 153, 2006.
- [7] T. Chirenje, Q.L. Ma and L. Liping, '*Retention of Cd, Cu, Pb and Zn by Wood Ash, Lime and Fume Dust*', Journal of Water, Air and Soil Pollution, Vol. 171, N°1-4, pp. 301 – 314, 2006.
- [8] L.Q. Ma, T.J. Logan and S.J. Traina, '*Lead Immobilization from Aqueous Solutions and Contaminated Soils using Phosphate Rocks*', Environment Science and Technology, Vol. 29, pp. 1118 – 1126, 1995.
- [9] J.J. Middelburg and R.N.J. Comans, '*Sorption of Cadmium on Hydroxyapatite*', Chemical Geology, Vol. 90, pp. 45 – 53, 1991.
- [10] Y. Xu and F.M. Schwartz, '*Lead Immobilization by Hydroxyapatite in Aqueous Solutions*', Journal of Contaminant Hydrology, Vol. 15, pp. 187 - 206, 1994.
- [11] X. Chen, J.V. Wright, J.L. Concha and L.M. Peurrung, '*Effects of pH on Heavy Metal Sorption on Mineral Apatite*', Environment Science and Technology, Vol. 31, pp. 624 – 631, 1997.

- [12] J. Jeanjean, U. Vincent and M. Fedoroff, 'Structural Modification of Calcium Hydroxyapatite Induced by Sorption of Cadmium Ions', *Journal of Solid State Chemical*, Vol. 108, pp. 68 – 72, 1994.
- [13] S. Zairi, K. Reybier, N. Jaffrezic-Renault, C. Martelet, B. Fabrys, 'Enhanced Ionodetection by Using Polyet-Hyleneimine as an Insulator Material', *Materials Science and Engineering C*, Vol. 21, pp. 35 – 41, 2002.
- [14] Y. Tsujimura, M. Yokohama and K. Kimura, 'Comparison between Silicone-Rubber Membranes and Plasticized poly(vinyl chloride) membranes containing calyx [4] arene ionophores for sodium ion-sensitive field-Effect Transistors in Applicability to Sodium Assay in Human Body Fluids', *Sensors and Actuators B: Chemical*, Vol. 22, N°3, pp. 195 – 199, 1995.
- [15] S.S. Levichev, A.V. Bratov and Y.G. Vlasov, 'New Photocurable Composition for ISFET Polymer Membranes', *Sensors and Actuators B: Chemical*, Vol. 19, N°1-3, pp. 625 – 628, 1994.
- [16] E. Davini, G. Mazzamurro and A.P. Piotta, 'Lead-Selective FET: Complexation Selectivity of Ionophores Embedded in the Membrane', *Sensors and Actuators B: Chemical*, Vol. 7, N°1-3, pp. 580 – 583, 1992.
- [17] A. Bouafsoun, S. Helali, S. Mebarek, C. Zeiller, A.F. Prigent, A. Othmane, A. Kerkeni, N. Jaffrézic-Renault and L. Ponsonnet, 'Electrical Probing of Endothelial Cell Behaviour on a Fibronectin/Polystyrene/Thiol/Gold Electrode by Faradaic Electrochemical impedance spectroscopy (EIS)', *Bioelectrochemistry*, Vol. 70, N°2, pp. 401 – 407, 2007.
- [18] N. Bezzi, D. Merabet, N. Benabdeslem and H. Arkoub, 'Caracterisation Physico-Chimique du Minerai de Phosphate de Bled El Hadba – Tebessa', *Annales de Chime – Sciences des Matériaux*, Vol. 26, N°6, pp. 5 – 23, 2001.