

## Electrochemical Sensors for Vanadium Determination

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**Abstract:** This paper is dedicated to the problem of vanadium (V) determination by the means of voltammetry. The comparison of results obtained for two types of sensor: volume glassy-carbon electrode and screen printed carbon electrode are presented. The experimental data is recorded using the hardware and software of «Novocontrol» (Germany): electrochemical interface POT/GAL 15V 10A, frequency response analyzer Alpha-A, and software for data collection and data processing WinDETA. Two three-electrode cells has been studied: for the first one the bulk glassy carbon electrode, and for the second one the screen printed electrodes has been used as the working electrode. In the first case the reference electrode has been made from silver chloride and the counter electrode from steel wire. In case of the screen printed electrodes, the electrodes were placed on the same plate. The peak of vanadium (V) was obtained under the potential of 1.3 V. It was found that the growth of the vanadium concentration increases magnitude of the cathode current measured then the mentioned potential is applied. The screen printed carbon electrodes provides better sensitivity in comparison with the volume glassy-carbon electrodes due to the more explicit vanadium potential peak.

**Keywords:** Vanadium (V), Volume Glassy-Carbon Electrode, Screen Printed Carbon Electrode, Voltammogram.

### 1. INTRODUCTION

Vanadium has strong impact on the environment due to several factors: bioaccumulation of this metal in living organism such as mushrooms can take place as well it can play a role of a cofactor in metalloenzymes of macroalgae, fungi and bacteria [1]. Therefore, the determination of trace vanadium level in environments, especially in deposit environments, becomes increasingly important.

The present paper is dedicated to development of electrochemical sensors allowing detection and determination of vanadium.

### 2. MEASUREMENT PROCEDURE

#### 2.1. Electrochemical interface and electrodes

A measuring system: «The broadband dielectric spectrometer Novocontrol BDS Concept 80» [2], working in conjunction with an electrochemical interface measurement system is used in



the experiment. The core of the installation was the electrochemical interface POT/GAL 15V 10A of «Novocontrol» (Germany) [3], working in conjunction with the frequency response analyzer Alpha-A and software for the collection and data processing WinDETA. The technical characteristics of the installation (wide frequency range from  $10^{-6}$  to  $10^6$  Hz, adjustable amplitude of DC and AC signals, high accuracy current and voltage measurement, automation of data acquisition and data processing) makes the installation an optimal solution to study complex electrochemical, corrosion processes, physical and chemical properties of various type of the surface layers and materials. The interface is connected to the measuring unit. For the determination of vanadium  $V^{5+}$  and a three-electrode cell of several different types of electrodes were used.

#### Working Electrode

Selection of the working electrode for metal concentration measurement depends on the nature of the metal, i.e. the potential ranges and mechanisms of reduction or oxidation. Mercury electrodes are suitable for the determination of more electronegative metals in the potential range from +0,2 V to -2,5 V. The graphite electrodes is used in the potential range from +1,5 V to 0,7 V [4] and they allows to determine the noble metals, as well as the more electronegative metal, in case of elimination of the interaction between them. Therefore, the volume glassy carbon electrode (fabricated by R&D Company «TomAnalyte», Tomsk, Russian Federation) is used as working electrode. The advantage of this material is a high chemical and electrochemical inertness in aqueous solutions of backgrounds.

#### Reference Electrode

The potential of the reference electrode must remain practically constant during the experiment. The composition of the reference electrode should not have an impact on the test solution, and vice versa. A silver chloride electrode [5] has been used. Silver chloride electrode consists of a coiled silver wire coated with sparingly soluble salt AgCl and lowered in KCl solution with precisely known concentration. For separating the reference electrode from the solution under test it was placed in the glass tube closed by a diaphragm from a material with low resistance (filter, porous glass, asbestos fiber).

#### Counter (Auxiliary) Electrode

An auxiliary electrode should be chemically and electrochemically inert in the test solution and be able to operate in a wide range of working potentials of the background solution. In addition, the products of the electrochemical reaction at the auxiliary electrode should not have influence on the electrochemical processes taking place at the working electrode. A steel wire was used as auxiliary electrode in frame of the present work.

#### Screen Printed Electrodes

Miniaturization of the electrochemical cell and electrodes are used, which provides the two-electrode or three-electrode system for the minimum area in one plane with the optimum distance between the electrodes. The advantages of this design is reducing experimental time and accurate sampling [6,7]. Measurements have been implemented by using screen printed carbon electrodes fabricated by IMAGES, Perpignan, France [8]. Such electrodes comprises chemically inert substrate; screen printed working, reference, and auxiliary electrodes; screen printed protection paste; working electrode incubation with the analyte of interest (IMAGES, Perpignan, France)

The reference electrode was preincubated in a saturated solution of potassium chloride KCl 0,1 M during 12 hours. Ammonium chloride solution  $\text{NH}_4\text{Cl}$  was used as a supporting electrolyte. Working electrode, counter electrode and screen printed electrode have been kept in the supporting electrolyte during 2 hours at room temperature. Measurements have been made for different concentrations of vanadium in the range from 0.005 mg/l to 1 mg/l.

## 2.2. Measurement with Volume Glassy-Carbon Electrode

In this experiment, the volume glassy-carbon electrode in a three-electrode cell has been used for the determination of vanadium  $\text{V}^{5+}$ . Ten cyclic voltammograms has been measured by means of linear scanning in the range of potentials from -1,6 V to +1,6 V for each concentration of vanadium (Fig. 1).

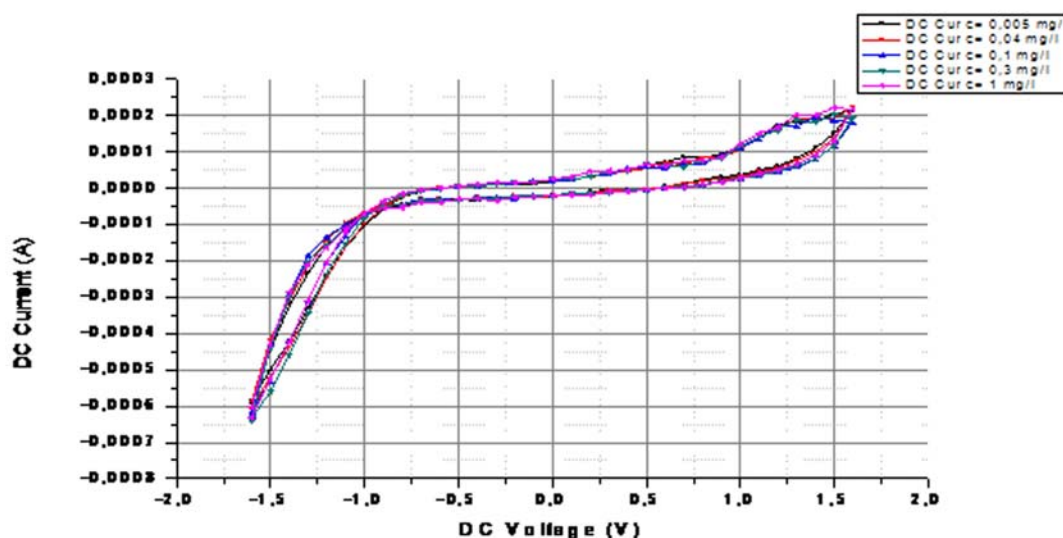


Figure 1. Voltammograms for volume glassy carbon electrodes

In the interval between 1.0 and 1.5 V peak of voltammograms were installed. Identified half-wave potential ( $E_{1/2}$ ) equal to 1.3 V has been associated with vanadium. The calibration dependency of the limit current on the concentration of the substance  $I(C)$  was constructed for this half-wave potential (Fig. 2).

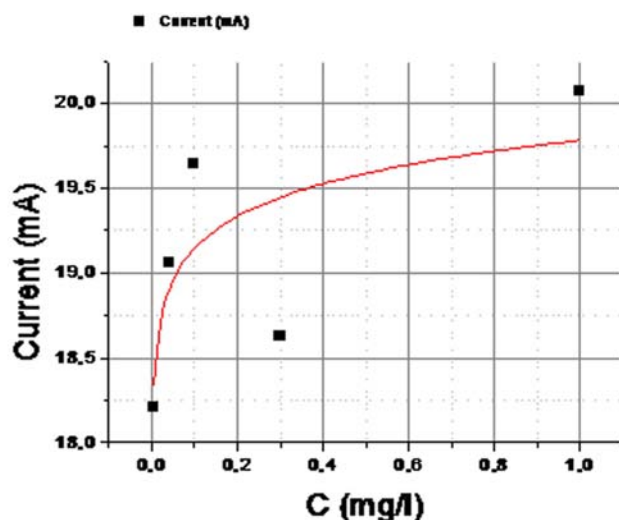


Figure 2. The calibration curve  $I(C)$  for the electrodes in the cell with the volume glassy-carbon electrode

The experimental points have been approximated by the Fick's law [4] for calculating of the limit current as the equation parameters. It has been founded that parameter  $K$  is equal to 19.78, the value of degree is 0.01. Therefore we can conclude that the processes on the volume glassy-carbon electrode have a mixed diffusion-kinetic and catalytic character.

### 2.3. Measurement with Screen Printed Carbon Electrode

In this experiment, the determination of vanadium  $V^{5+}$  has been implemented by means of screen printed carbon electrode. Ten cyclic voltammograms has been measured by means of linear scanning in the range of potentials from -1,6 V to +1,6 V for each concentration of vanadium (Fig. 3).

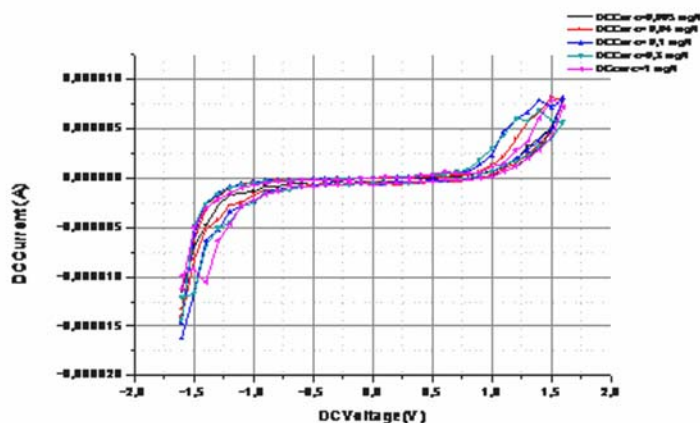


Figure 3. Voltammograms for screen-printed carbon electrodes

The experimental points (Fig. 4) have been approximated by the Fick's law [4] for calculating of the limit current as the equation parameters. It has been founded that parameter  $K$  is equal to 7.89, the value of degree  $n$  is 0.13. Therefore we can conclude that the processes on the screen printed carbon electrode have a mixed diffusion-kinetic and catalytic character.

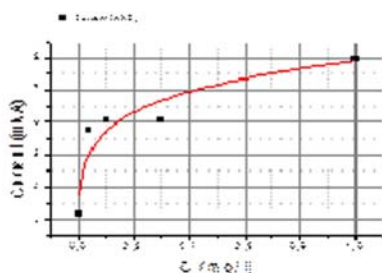


Figure 4. The calibration curve  $I(C)$  for the screen printed carbon electrode

### 3.CONCLUSION

For solid electrodes, the mixed diffusion-kinetic and catalytic currents ( $0 < n < 1$ ) has been established. In the case of screen printed electrodes the contribution of adsorption and catalytic currents is weaker. It can be probably explained by the facts of the smaller surface area and lower sorption capacity of the material.

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