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An innovative micrometric granular graphite–glass system composite electrode "ready to use" in voltammetry techniques

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ABSTRACT

A low cost composite electrodes employing tellurite oxide, vanadium oxide and micrometric granular graphite (NWE), were designed as an alternative to be used as working electrode in voltammetry techniques. The synthesis of these composite electrodes is carried out easily; in a short time and their surface not require previous preparation. X-ray diffraction, X-ray fluorescence spectrometry and optical microscopy studies were used to determine the morphology and chemical composition of these electrodes. The conductivity characterization was conducted with impedance and electrochemical measurements. The electrochemical properties of NWE were studied using potassium hexacyanoferrate (II) and ascorbic acid system.

1. Introduction

The selection of a working electrode to be used in voltammetric techniques is important for its employ in different fields (analytical chemistry, biochemistry, pharmacology, medicine). Effective electrodes are the key to successful development of a system. The working electrodes should have a low ohmic resistance and be resistant to chemical and biological fouling. Thus, they should exhibit favorable electrochemical behavior with the analyte, reproducible electron transfer, a defined potential window, ease of reproduction of the electrode surface, high mechanic resistance, and low cost [1]. Taking into account these properties is important to choose the right material to enable the development of electrodes with desired geometries and fast surface renewal after a measurement. Generally the materials used for working electrodes include platinum [2], gold [3], mercury, glassy carbon [4,5] and semiconductors. Nowadays different materials are used for preparing modified electrodes and electrodes composites (carbon nanotubes [6], ionic liquids [7], titanate nanotubes [8], chitosan [9], bismuth [6], nanoparticles [10], graphite [11] and conducting polymers [12,13]). There are several works in the literature which employ composite materials for development of electrical devices such as electrodes [14–16]. Composite electrodes can be defined as a material consisting of at least one conductor phase mixed with at least one insulator phase, with different complementary properties (chemical, mechanical and physical). The advantages of these electrodes include its versatility to obtain different sizes, shapes and configurations, shows a higher signal to noise ratio to the corresponding pure conductive electrode, etc. [1].

The design of this type of electrodes using new materials that are economical, easy to prepare and does not require surface treatment, would contribute to the electroanalytical methods, replacing conventional electrodes. Within these materials, tellurite oxide glass containing transition metals show interesting electrical transport properties. In the literature have been reported several studies of glassy systems prepared by tellurite oxide with different modifiers oxides, as V_2O_5, MoO_3, CuO, etc., which alter the network structure and involve particular properties as their electrical behavior [17–19]. Although, tellurite oxide glasses modified by vanadium oxide showed semiconductor properties, exhibits a somewhat high resistance at room temperature to be used as working electrode in electroanalytical techniques. The addition of a conductor phase will improve the conductive properties.

This paper shows a quick, easy and low cost method to synthesize composite electrodes employing instruments generally available in routine laboratories. For this purposed a glass system of tellurite oxide (as network former), vanadium oxide (as network modifier) and micrometric granular graphite in order to enhance conductivity, was designed and studied to be used in voltammetric techniques. These composite electrodes does not require surface activation such as polishing on with some types of abrasive

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containing pads and sonication to remove remains of polishing material. Thus, "electrodes ready to use" were synthesized.

2. Experimental

2.1. Reagents

All reagents were of analytical grade: tellurite oxide (99.999% Sigma–Aldrich), vanadium oxide (99.9% Cerac), potassium hexacyanoferrate (II) trihydrate (Sigma–Aldrich), potassium chloride (Merck), ascorbic acid (Sigma) and 0.050 M phosphate buffer pH 7.40. Commercial micrometric granular graphite was employed. To prepare the solutions, ultrapure water (18 MΩ cm^{-1}) supplied by a Milli-Q system was used.

2.2. Instrumentation

The X-ray diffraction was performed with PW1710 BASED in continuous scan mode with a copper anode and 45 KV–30 mA for the tension and electrical current generator respectively. The samples were exposed to the Cu Kα radiation (λ = 1.54 Å) at room temperature in the 2θ range: 3°–60°.

In order to determine the glassy system composition X-ray fluorescence spectrometry was carried out by employing a PANalytical MagiíX spectrofluorimeter (Rhodium anode, Helium atmosphere, LiF crystals 200 and 220, PX1, PX4, PE and flow detector).

Glassy system images were obtained with a Nikon Eclipse E-200 POL polarizing optical microscope.

The samples were polished with very fine sand papers in order to obtain glass disks with two parallel faces of thickness ranging between 0.4 and 1.2 mm. Each sample was coated uniformly with a thin layer of silver paint with the purpose of having proper electrical contact. Impedance measurements were carried out with an Agilent 4284A LCR meter in frequency range from 20 Hz to 1 MHz in the temperature domain from 25 to 50 °C.

Cyclic voltammetry (CV) experiments were performed using an Epsilon potentiostat (BASi-Bioanalytical System, USA) and run with electrochemical analysis software. A three-electrode configuration consisting of new working electrode (NWE), Ag/AgCl (3 M NaCl) and a platinum foil as working, reference and counter electrodes respectively were used.

2.3. Synthesis of glassy system

In order to synthesize glassy systems prepared by tellurite oxide, vanadium oxide and micrometric granular graphite, the "quenching melting technique" was employed. The system developed is according to the following formulation: $xC[0.6V_2O_5\ 0.4TeO_2]$, (x = 0, 1, 2, 3, 4, 6 and 8%) [17,18]. For this proposed an appropriate amounts of tellurite and vanadium oxides and different percentages of micrometric granular graphite were mixed in an open porcelain crucible. The mix was melted at 850 °C in an electric furnace during 45 min and homogenized every 15 min. A portion of the melt was poured in small portions into a preheated aluminum plate and allowed to cool to room temperature. The formed drops were used for morphological studies. For this proposed these drops were pulverized in agate mortar for X-ray diffraction, X-ray fluorescence spectrometry and optical microscopy studies.

On the other hand, the tips of platinum wires were introduced in the different systems, so as to obtain homogeneous small drops and allowed to cool to room temperature. Thereby new working electrodes (NWE) were obtained to be used in electrochemical analysis: NWE0, NWE1, NWE2, NWE3, NWE4, NWE6 and NWE8 corresponding to a micrometric granular graphite content of 0, 1, 2, 3, 4, 6 and 8%, respectively. Thereby, it is possible to obtain electrodes quickly, easily and "ready to use".

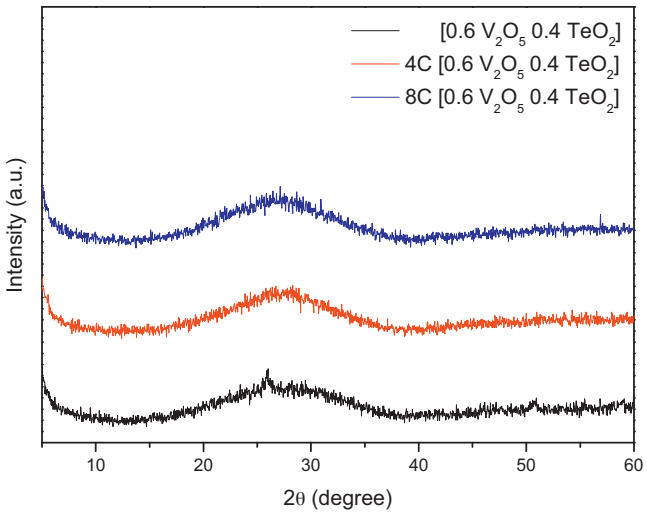

Fig. 1. X-ray diffraction patterns for glassy systems with and without graphite particles.

3. Results Discussion

3.1. Granular graphite characterization

In order to obtain graphite particle size, measurements by Laser Scattering Particle Size Distribution Analyzer LA-950 was conducted. The average particle size obtained was 36.7 microns.

3.2. Glassy system characterization

3.2.1. Morphological analysis

The amorphous character of the resulting solid glassy system was tested by X-ray diffraction. Fig. 1 shows X-ray diffraction patterns for glassy system with and without added graphite particles. The absence of sharp and intense peaks, characteristic of crystalline materials, indicates that crystallization did not occur. This confirms that the synthesized material is a glass material and that the incorporation of graphite does not modify the state of the material. In this figure, the peak characteristic of graphite are not observed due the sensitivity of the technique is not appropriate to solve the low percentage of this phase.

X-ray fluorescence spectrometry analysis indicated the presence of vanadium and tellurium, which are the main components of the system. Furthermore, silicon, zirconium and molybdenum were detected as impurities due to the use of commercial graphite (Fig. 2).

Fig. 3 shows a microphotograph in which the graphite particles are randomly dispersed in the glass matrix.

To investigate the electrical conduction characteristics, the module of the impedance (Z) and phase angle (ϕ) of each system have been measured as function of frequency.

Electrical conductivity increases with increasing temperature and we can represent this relation with Arrhenius-type equation as:

$$\sigma_{dc} = \frac{\sigma_0}{T} e^{-(E_a/KT)}$$

where E_a is the activation energy of the conductivity, σ_0 is the preexponential factor and KT have the usual meaning.

Nyquist plots of the developed systems at different temperatures were carry out. A typical plot is shown in Fig. 4. The resistance