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## **An innovative micrometric granular graphite–glass system composite electrode “ready to use” in voltammetry techniques**

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### Highlights

> An innovative composite electrodes (NWE) “ready to use” were developed > Micrometric granular graphite-glass system was employed for the synthesis > NWE electrodes are low cost and easy to generate > NWE electrodes does not require prior surface activation > These electrodes are an alternative to be used as working electrodes in voltammetry

### 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.

**Keywords:** Graphite–glass system; Composite electrode; Low cost electrode fabrication; Voltammetry

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## 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

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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 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 ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) 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  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at room temperature in the  $2\theta$  range:  $3^\circ$ -  $60^\circ$ .

In order to determine the glassy system composition X-ray fluorescence spectrometry was carried out by employing a PANalytical Magi'X 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  $25^\circ\text{C}$  to  $50^\circ\text{C}$ .

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 (3M 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:  $x\text{C}[0.6\text{V}_2\text{O}_5 \cdot 0.4\text{TeO}_2]$ , ( $x=0, 1, 2, 3, 4, 6$  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  $850^\circ\text{C}$  in an electric furnace during 45 minutes and homogenized every 15 minutes. 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".

### **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. Figure 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.

Figure 1

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 (Figure 2).

Figure 2

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

Figure 3

To investigate the electrical conduction characteristics, the module of the impedance ( $Z$ ) and phase angle ( $\phi$ ) 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:

$$\sigma_{dc} = \frac{\sigma_0}{T} e^{-\left(\frac{Ea}{KT}\right)}$$

where  $E_a$  is the activation energy of the conductivity,  $\sigma_0$  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 Figure 4. The resistance data were obtained, allowing to calculate conductivity values at each temperature ( $\sigma_T = \text{cell geometric factor} \times R_T^{-1}$ ). [20]. Glassy systems will be used as working electrodes in aqueous solutions thereby the temperature range studied was appropriate for this medium. The obtained results indicate that an increase in temperature produced a decrease in the resistance.

Figure 4

On the other hand, Figure 5 shows the isotherm of conductivity response as a function of the molar fraction of graphite, at 298 K. This figure confirms that the system with micrometric granular graphite content of 6% has the best electrical response to the application as electrode. The systems with higher graphite percentages than 8% could not be analyzed because they have low mechanical strength. It is observed that the conductivity values of the synthesized glassy system are lower than carbon electrode materials commonly used [21]. Rui et al. observed the same behavior when low concentration of carbon is added in a glassy system [22].

Figure 5

### 3.2.2. Electrochemical characterization

The response of  $2.5 \times 10^{-3} \text{ mol L}^{-1}$  potassium hexacyanoferrate solution in  $0.1 \text{ mol L}^{-1}$  KCl as supporting electrolyte using cyclic voltammetry, was analyzed with all of the new working electrodes. This study was carried out at different scan rates from



10 to 100 mV s<sup>-1</sup>. Amazingly despite the low conductivity of these materials, they have a good response to this redox couple. Table 1 shows  $E_{pa}$ ,  $E_{pc}$ ,  $\Delta E$ ,  $J_{pa}$ ,  $J_{pc}$  values at 10, 25, 50 and 100 mV s<sup>-1</sup>, employing NWE4, NWE6 and NWE8 electrodes. It can be observe that anodic and cathodic peak potential vs. Ag/AgCl-RE, vary with scan rate. Note that an increase in the percentage of graphite generate a decrease in  $\Delta E$  at the same scan rate, indicating that the most reversible and the fastest electron transfer electrochemical reaction occurs at NWE8 electrode. Besides, the three electrodes anodic peak currents increase with increasing scan rate and the  $I_{pa}$  is proportional to the square root of  $v$ , indicating that the redox process of the potassium hexacyanoferrate is diffusion controlled. For example for NWE6, the regression equation is  $I_{pa} = 0.061 v^{1/2} - 0.015$  ( $R^2=0.999$ ). Furthermore, the peak current ratio of anodic to cathodic peak ( $I_{pa}/I_{pc}$ ) remains almost one for all tested scan rates.

Table 1

Figure 6 shows a cyclic voltammograms (Current density vs Potential vs. Ag/AgCl-RE) using NWE4, NWE6 and NWE8 electrodes recorded between -0.20 and +0.80 V vs. Ag/AgCl-RE at different scan rates (10, 25, 50 and 100 mV s<sup>-1</sup>). The anodic and cathodic peak potentials and the peak potential difference ( $\Delta E$ ) were calculated from the cyclic voltammograms. As can be seen in the studied systems a higher scan rates the peak potential difference increases. Furthermore, when the percentage of graphite in each system is increased the voltammograms are more defined and anodic and cathodic potential peaks are closer at a given scan rate.

The peak-to-peak separation is directly correlated to the electron transfer kinetic, these findings indicate that the most reversible and the fastest electron transfer electrochemical reaction occurs at NWE8 electrode.

Analyzing the performance of the electrodes NWE0, NWE1, NWE2 and NWE3, the anodic/cathodic peak currents ( $I_{pa}$ ,  $I_{pc}$ ) of the potassium ferro/ferricyanide redox couple were not observed, probably due to the low content of graphite particles which are the responsible for conduction properties.

Figure 6

Table 2 shows electrochemical parameters at different scan rates, of commercial electrodes (highly oriented pyrolytic graphite and glassy carbon) using potassium ferro/ferricyanide redox couple. As can be seen the current density values of NWE electrodes (Table 1) are comparable with those of commercial electrodes. The peak-to-peak separations in NWE electrodes are larger than commercial electrodes due to a lower kinetics of the electron transfer process. The sluggish charge transfer is demonstrated with the resistive appearance of the voltammetric profiles (Figure 6).

Table 2

On the other hand the cyclic voltammetry behavior of ascorbic acid system was carried out. Ascorbic acid solution in phosphate buffer pH 7.40 as supporting electrolyte was analyzed with NWE4, NWE6 and NWE8. This study was performed at different scan rates from 10 to 100  $\text{mV s}^{-1}$ . Table 3 shows the electrochemical study of the proposed and commercial electrodes (highly oriented pyrolytic graphite and glassy carbon). In all cases, the oxidation peak current ( $I_{pa}$ ) of ascorbic acid increased with increase in scan rate. In the NWE electrodes, the linear relationship between  $I_{pa}$  and  $v^{1/2}$  demonstrates that the electrochemical oxidation of ascorbic acid are diffusion-controlled process. The regression equation is  $I_{pa} = 3.37 v^{1/2} - 0.34$  ( $R^2=0.996$ ) for NWE6. Comparing NWE and commercial electrodes, anodic peak potential vs. Ag/AgCl-RE, show a similar behavior with increasing scan rate. Note that the current density values and  $E_{pa}$  of NWE are comparable with those of commercial electrodes. Figure 7 shows the cyclic voltammograms employing NWE6 at different scan rates.

Table 3

Figure 7

#### 4. Conclusions

Innovative micrometric granular graphite-glass system composite electrodes have developed with tellurium and vanadium oxide and different percentages of graphite particles. Morphological and electrochemical studies of the synthesized glassy system show that is a good material to design composites electrodes. The new working electrodes (NWE) are easy to generate and does not require surface activation. Thus, composite electrodes "ready to use" were synthesized. Furthermore, they exhibit good electrochemical performance, comparable to the commercial electrodes. A further advantage is that they are two hundred times cheaper than glassy carbon electrodes. These studies confirm that they may be an alternative for use as composites working electrodes in voltammetric techniques.

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#### References

- [1] J. Wang, Analytical Electrochemistry, third ed., J. Wiley & Sons, New Jersey, 2006.
- [2] S. Mondal, M.V. Sangaranarayanan, A novel non-enzymatic sensor for urea using a polypyrrole-coated platinum electrode, Sensors and Actuators B 177 (2013) 478.

- [3] M. Cho, L. Chun, M. Lin, W. Choe, J. Nam, Y. Lee, Sensitive electrochemical sensor for detection of lipopolysaccharide on metal complex immobilized gold electrode, *Sensors and Actuators B* 174 (2012) 490.
- [4] A. Babaei, A. R. Taheri, Nafion/Ni(OH)<sub>2</sub> nanoparticles-carbon nanotube composite modified glassy carbon electrode as a sensor for simultaneous determination of dopamine and serotonin in the presence of ascorbic acid, *Sensors and Actuators B* 176 (2013) 543.
- [5] A. Kumaravel, M. Chandrasekaran, Nanosilver/surfactant modified glassy carbon electrode for the sensing of thiamethoxam, *Sensors and Actuators B* 174 (2012) 380.
- [6] G. D. Pierini, A. M. Granero, M. S. Di Nezio, M. E. Centuri3n, M. A. Zon, H. Fern3ndez, Development of an electroanalytical method for the determination of lead in Argentina raw propolis based on bismuth electrodes, *Microchemical Journal* 106 (2013) 102.
- [7] M. Opalloa, A. Lesniewski, A review on electrodes modified with ionic liquids, *Journal of Electroanalytical Chemistry* 656 (2011) 2.
- [8] H. Dai, H. Xu, X. Wu, Y. Lin, M. Wei, G. Chen, Electrochemical behavior of thionine at titanate nanotubes-based modified electrode: A sensing platform for the detection of trichloroacetic acid, *Talanta* 81 (2010) 1461.
- [9] F. Kuralay, T. Vural, C. Bayram, E. Baki Denkb3as, S. Abaci, Carbon nanotube–chitosan modified disposable pencil graphite electrode for Vitamin B<sub>12</sub> analysis, *Colloids and Surfaces B: Biointerfaces* 87 (2011) 18.
- [10] A. M. Ashrafi, S. Cerov3cb, S. Mudric, V. Guzsv3ny, L. Hus3kov3, I. Urbanov3, K. Vytras, Antimony nanoparticle-multiwalled carbon nanotubes composite immobilized at carbon paste electrode for determination of trace heavy metals, *Sensors and Actuators B* 191 (2014) 320.
- [11] A. R. Khaskheli, J. Fischer, J. Barek, V. Vyskocil, Sirajuddin, M.I. Bhangar, Differential pulse voltammetric determination of paracetamol in tablet and urine samples at a micro-crystalline natural graphite–polystyrene composite film modified electrode, *Electrochimica Acta* 101 (2013) 238.

- [12] Mei-Rong Huang, Yong-Bo Ding and Xin-Gui Li, Lead-ion potentiometric sensor based on electrically conducting microparticles of sulfonic phenylenediamine copolymer, *Analyst* 138 (2013) 3820.
- [13] Xin-Gui Li, Hao Feng, Mei-Rong Huang, Guo-Li Gu, and Mark G. Moloney, Ultrasensitive Pb(II) Potentiometric Sensor Based on Copolyaniline Nanoparticles in a Plasticizer-Free Membrane with a Long Lifetime, *Anal. Chem.* 84 (2012) 134.
- [14] J. Manso, M.L. Mena, P. Yáñez-Sedeño, J. Pingarrón, Electrochemical biosensors based on colloidal gold–carbon nanotubes composite electrodes, *Journal of Electroanalytical Chemistry* 603 (2007) 1.
- [15] J. Ping, Y. Wang, J. Wu, Y. Ying, F. Ji, Determination of ascorbic acid levels in food samples by using an ionic liquid–carbon nanotube composite electrode, *Food Chemistry* 135 (2012) 362.
- [16] I. Cesarino, V. Cesarino, M. R.V. Lanza, Carbon nanotubes modified with antimony nanoparticles in a paraffin composite electrode: Simultaneous determination of sulfamethoxazole and trimethoprim, *Sensors and Actuators B* 188 (2013) 1293.
- [17] E.C. Cardillo, R.A. Montani, M.A. Frechero, A weak mixed mobile ion effect in vanadium–tellurite oxide glass modified by silver and lithium cations, *Journal of Non-Crystalline Solids* 356 (2010) 2760.
- [18] N. Lebrum, M. Levy, J.L. Souquet, Electronic conductivity in glasses of the  $\text{TeO}_2\text{-V}_2\text{O}_5\text{-MoO}_3$  system, *Solid State Ionics* 40 & 41 (1990) 718.
- [19] E.C. Cardillo, S. TERNY, M.A. Frechero, Enthalpy relaxation of the glassy matrix in vanadium–molybdenum–tellurite oxide glasses, *Thermochimica Acta* 566 (2013) 10.
- [20] E. Barsoukov, J. R. Macdonald, *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2th. Ed. ISBN: 978-0-471-64749-2. Wesley.
- [21] R. L. McCreery, Advanced Carbon Electrode Materials for Molecular Electrochemistry, *Chemical Reviews* 108 (2008) 2646.

- [22] X. Rui, Q. Yana, M. Skyllas-Kazacos, T. M. Lim,  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  cathode materials for lithium-ion batteries: A review, *Journal of Power Sources* 258 (2014) 19.

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## Figure Captions

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

**Figure 2.** X-Ray fluorescence of  $x\text{C}[0.6\text{V}_2\text{O}_5 \cdot 0.4\text{Te}_2\text{O}]$  with different analyzer crystal: a) LiF 220, b) LiF200.

**Figure 3.** a) Microphotograph of the glassy system with 4 % of micrometric granular graphite (MGG) (400X magnification). b) Glassy system over nylon mesh with pore size of approximately 20  $\mu\text{m}$

**Figure 4.** Nyquist plot at different temperature for  $x\text{C} [0,6\text{V}_2\text{O}_5 \cdot 0,4\text{TeO}_2]$ .

**Figure 5.** Isotherm of conductivity response at 298 K as a function of the molar fraction of graphite.

**Figure 6.** Cyclic voltammograms of NWEs at different scan rates of potassium ferro/ferricyanide redox couple: a) NWE4, b) NWE6 and c) NWE8.

**Figure 7.** Cyclic voltammograms of NWE6 at different scan rates of ascorbic acid.

**Table 1.**  $E_{pa}$ ,  $E_{pc}$ ,  $\Delta E$ ,  $J_{pa}$ ,  $J_{pc}$  values at 10, 25, 50 and 100  $\text{mV s}^{-1}$ , employing potassium ferro/ferricyanide redox couple with NWE4, NWE6 and NWE8 electrodes.

Scan Rate [ $\text{mV s}^{-1}$ ]	NWE4					NWE6					NWE8				
	$E_{pa}$ [V]	$E_{pc}$ [V]	$\Delta E$ [V]	$J_{pa}$ [ $\mu\text{A.cm}^{-2}$ ]	$J_{pc}$ [ $\mu\text{A.cm}^{-2}$ ]	$E_{pa}$ [V]	$E_{pc}$ [V]	$\Delta E$ [V]	$J_{pa}$ [ $\mu\text{A.cm}^{-2}$ ]	$J_{pc}$ [ $\mu\text{A.cm}^{-2}$ ]	$E_{pa}$ [V]	$E_{pc}$ [V]	$\Delta E$ [V]	$J_{pa}$ [ $\mu\text{A.cm}^{-2}$ ]	$J_{pc}$ [ $\mu\text{A.cm}^{-2}$ ]
10	0.392	0.0601	0.33	123	-125	0.358	0.125	0.23	170	-184	0.324	0.140	0.18	113	-101
25	0.503	-0.0697	0.51	227	-225	0.435	0.0610	0.37	292	-304	0.381	0.100	0.28	191	-171
50	0.634	-0.173	0.81	328	-334	0.518	-0.0136	0.53	418	-423	0.442	0.0393	0.40	270	-250
100	0.773	-0.192	0.97	465	-433	0.636	-0.144	0.78	581	-582	0.526	-0.0421	0.57	383	-352

**Table 2.**  $E_{pa}$ ,  $E_{pc}$ ,  $\Delta E$ ,  $J_{pa}$ ,  $J_{pc}$  values at 10, 25, 50 and 100  $\text{mV s}^{-1}$ , employing potassium ferro/ferricyanide redox couple with highly oriented pyrolytic graphite and glassy carbon electrodes

Scan Rate [ $\text{mV s}^{-1}$ ]	Highly oriented pyrolytic graphite					Glassy carbon				
	$E_{pa}$ [V]	$E_{pc}$ [V]	$\Delta E$ [V]	$J_{pa}$ [ $\mu\text{A.cm}^{-2}$ ]	$J_{pc}$ [ $\mu\text{A.cm}^{-2}$ ]	$E_{pa}$ [V]	$E_{pc}$ [V]	$\Delta E$ [V]	$J_{pa}$ [ $\mu\text{A.cm}^{-2}$ ]	$J_{pc}$ [ $\mu\text{A.cm}^{-2}$ ]
10	0.277	0.181	0.096	167	-135	0.254	0.185	0.069	156	-126
25	0.286	0.172	0.11	257	-210	0.254	0.182	0.072	221	-221
50	0.295	0.168	0.13	373	-288	0.257	0.186	0.071	406	-368
100	0.310	0.155	0.15	524	-392	0.258	0.184	0.074	582	-510

**Table 3.**  $E_{pa}$  and  $J_{pa}$  values at 10, 25, 50 and 100  $mV s^{-1}$ , employing ascorbic acid system with NWEs, highly oriented pyrolytic graphite and glassy carbon electrodes.

Scan rate [ $mV.s^{-1}$ ]	NWE4		NWE6		NWE8		HPGO*		GC**	
	$E_{pa}$ [V]	$J_{pa}$ [ $\mu A.cm^{-2}$ ]	$E_{pa}$ [V]	$J_{pa}$ [ $\mu A.cm^{-2}$ ]	$E_{pa}$ [V]	$J_{pa}$ [ $\mu A.cm^{-2}$ ]	$E_{pa}$ [V]	$J_{pa}$ [ $\mu A.cm^{-2}$ ]	$E_{pa}$ [V]	$J_{pa}$ [ $\mu A.cm^{-2}$ ]
10	0.195	94.2	0.206	92.2	0.241	103	0.225	69.1	0.224	75.9
25	0.224	130	0.309	153	0.259	139	0.261	137	0.264	115
50	0.246	155	0.351	182	0.293	167	0.286	190	0.276	143
100	0.260	185	0.394	182	0.318	221	0.343	263	0.290	209

\* Highly oriented pyrolytic graphite

\*\* Glassy carbon

Figure 1

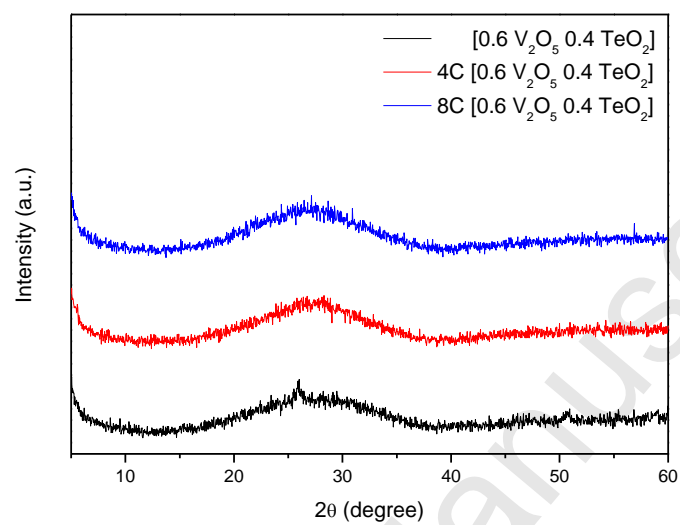
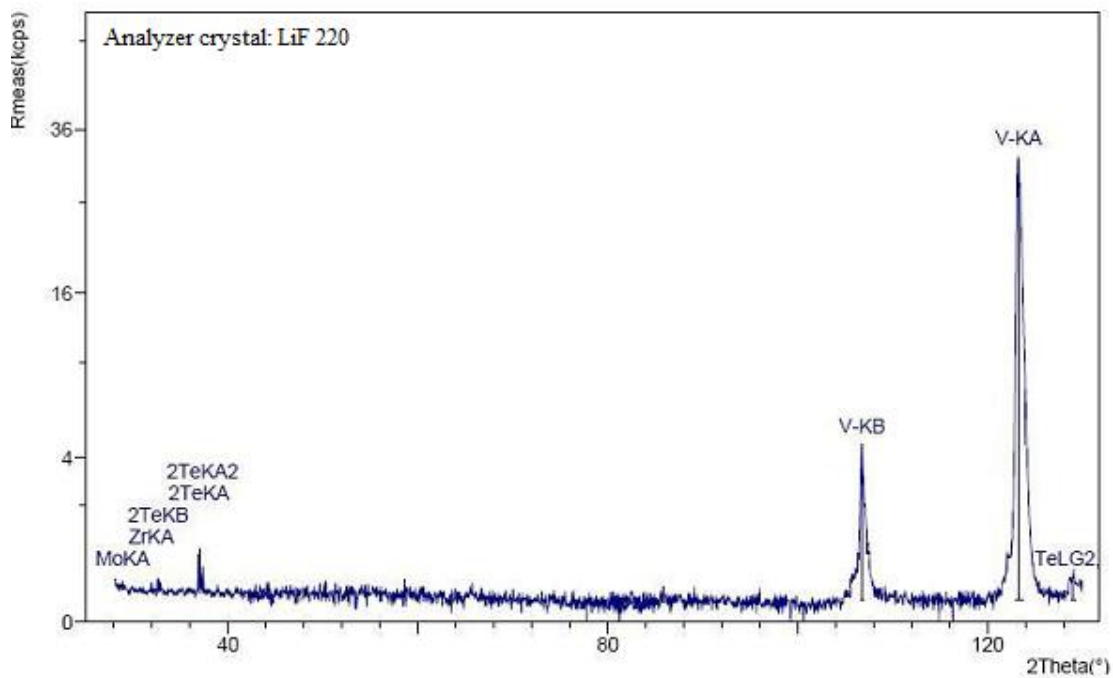


Figure 2

a)



b)

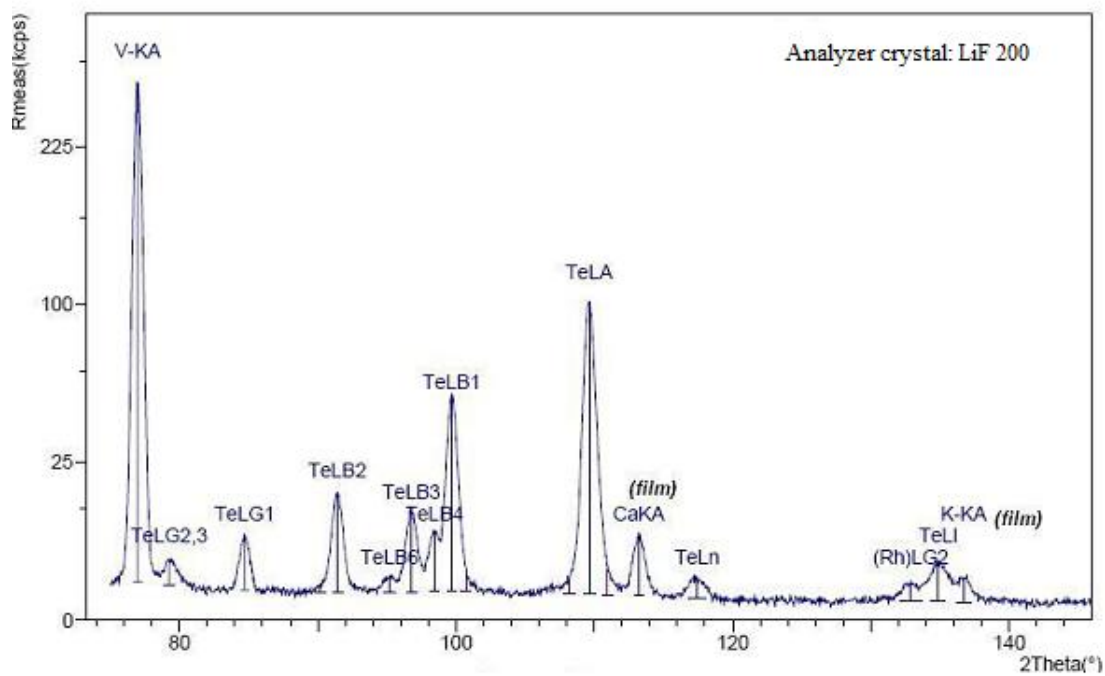


Figure 3

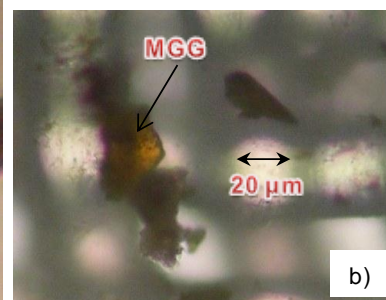
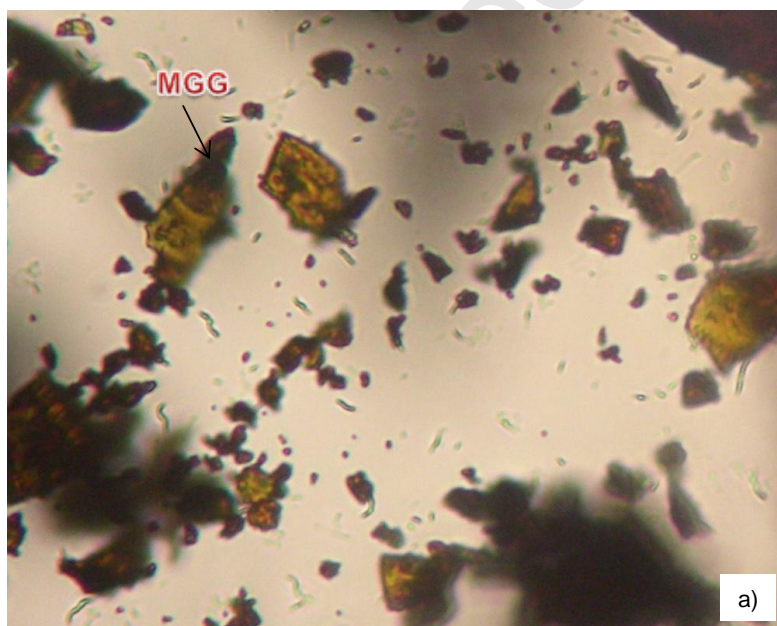


Figure 4

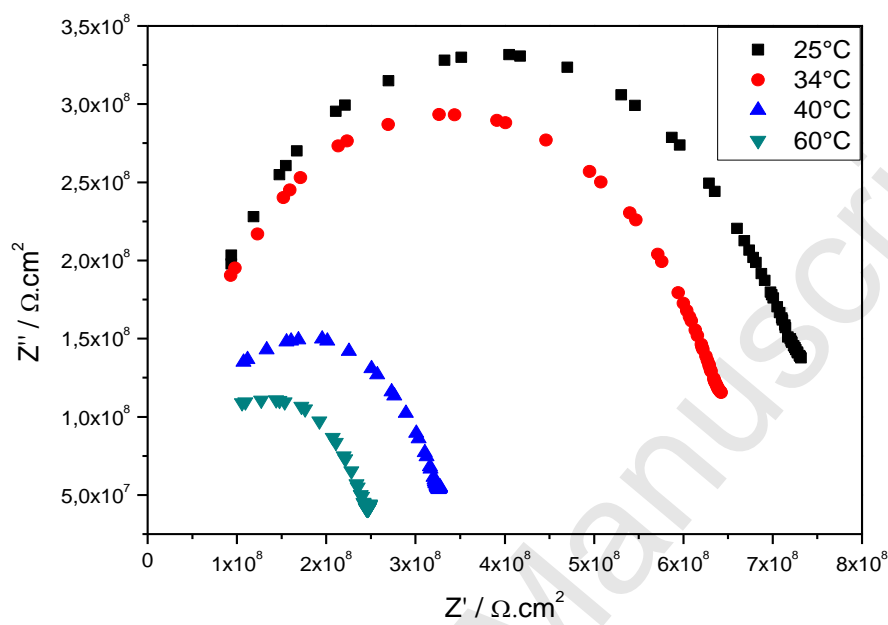


Figure 5

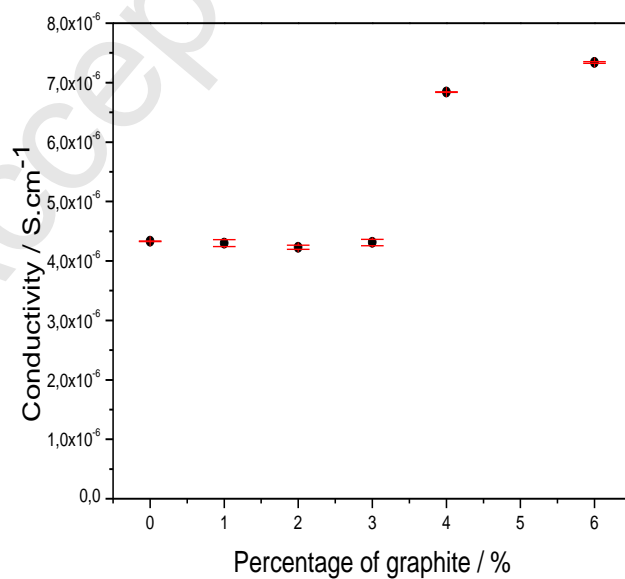
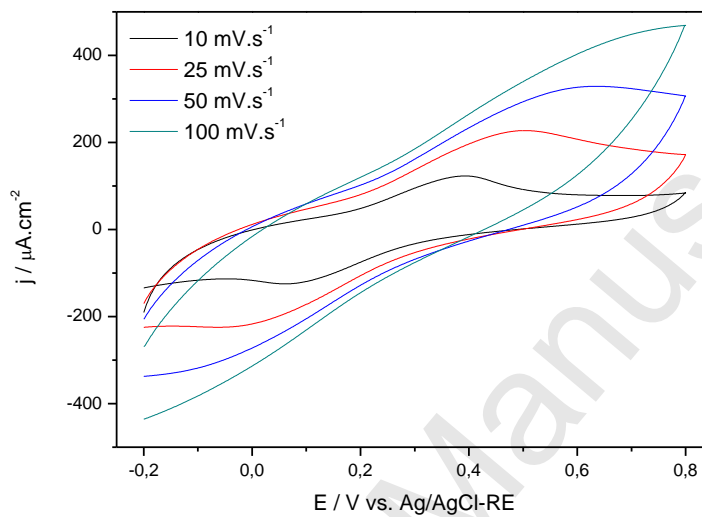
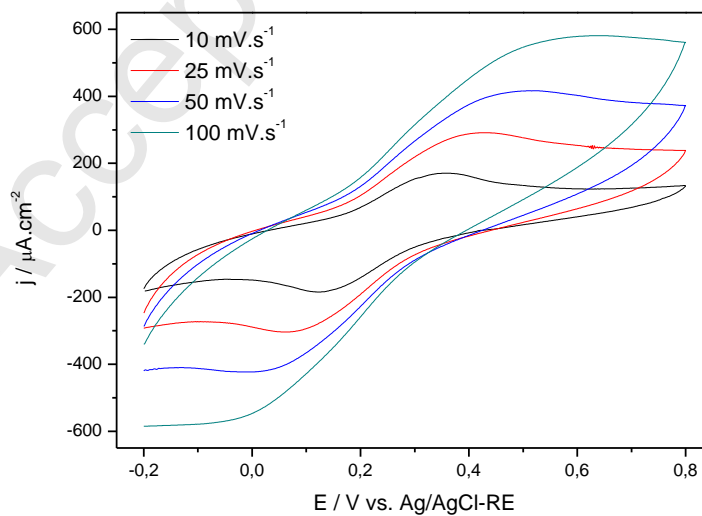


Figure 6

a)



b)





c)

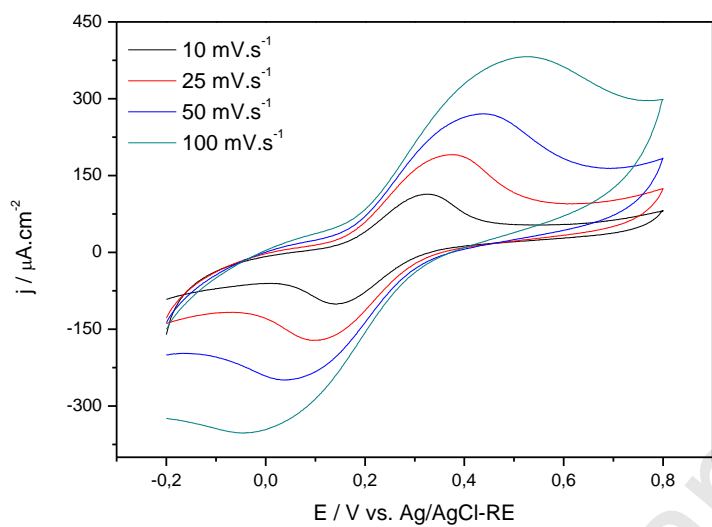


Figure 7

