

## ELECTRO-OXIDATION OF ASCORBIC ACID ON PEROVSKITE-MODIFIED ELECTRODES

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### Abstract

The main purpose of this research was to obtain LaMnO<sub>3</sub> perovskite-modified graphite electrodes, to characterise them and to observe their electrochemical behaviour in the presence of ascorbic acid. The morphology of the perovskite films were studied by scanning electron microscopy (SEM) and their double-layer capacitance was determined using cyclic voltammetry. The results are promising, but the electrocatalytic activity of the films for the oxidation of ascorbic acid needs to be improved.

### Introduction

Perovskite-type oxides have received extensive attention due to their high electronic conductivity, mobility of the oxide ions within the crystal, variations on the oxygen content, photocatalytic and magnetic properties, electrically active structure, chemical stability and thermoelectric and dielectric properties. They are widely used in the research of fuel cells, electrochemical sensors and as catalysts in oxidation and reduction processes [1]. Ascorbic acid (AA) is an important nutrient and most of the methods for quantifying it were developed based on its reducing properties. Electrochemical methods have gained the most success among the different techniques for quantifying the concentration of AA in solutions. AA is easily oxidized to dehydroascorbic acid and this reaction can be induced and monitored by cyclic voltammetry [2]. In the past, we reported a simple procedure for the preparation of carbon modified electrodes by the *slow evaporation* of a N,N-dimethylformamide (DMF) solution containing the catalyst. These electrodes were also used for the electro-oxidation of AA [3].

In the present work, we used a LaMnO<sub>3</sub> perovskite-type material, to modify the surface of graphite electrodes and we studied their electrochemical behaviour.

### Experimental

The electrochemical characterization of the LaMnO<sub>3</sub> powder was investigated in a conventional three-electrode cell equipped with a Pt wire counter electrode, an Ag/AgCl (sat. KCl) reference electrode and a modified graphite (G) disk electrode ( $S = 0.28 \text{ cm}^2$ ) as working electrode. The G disk was used as a substrate on which a thin layer of the perovskite was placed. The perovskite suspension was prepared by adding 10 mg of LaMnO<sub>3</sub> powder in 500  $\mu\text{L}$  of DMF. After 30 min in an ultrasonic bath, a volume of 15  $\mu\text{L}$  of the suspension was applied on the surface of the G disk and allowed to slowly evaporate. The SEM technique was employed to study and confirm the uniformity of the deposited layer (data not shown).

Electrochemical experiments were carried out using a potentiostat type Voltalab PGZ 402. The double-layer capacitance of the modified electrode – electrolyte interface was determined by recording cyclic voltammograms in 0.1 M KCl, at various scan rates between -0.2 and 0.2 V. The capacitive current density was calculated as the average of anodic and cathodic currents taken at a potential where only double-layer adsorption and desorption features were observed (0 V vs Ag/AgCl). The capacitance was obtained from the slope of the

linear dependence of capacitive current density *versus* scan rate [4]. The oxidation reaction of AA was carried out in 0.1 M KCl at a scan rate of 100 mV/s.

## Results and discussion

The characteristic voltammetric peak of AA in 0.1 M KCl solution appears at  $\sim 0.5$  V and is assigned to the oxidation of AA to dehydroascorbic acid (Figure 1).

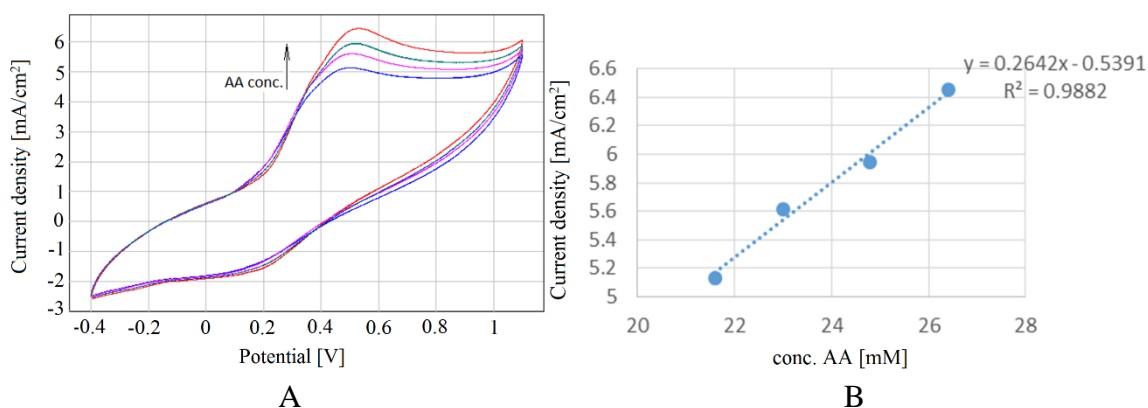


Figure 1. (A) Cyclic voltammograms obtained for the perovskite modified electrode at different ascorbic acid concentrations (21.6, 23, 24.8, 26.4 mM), in 0.1M KCl solution, at a scan rate of 100 mV/s. (B) The corresponding plot of anodic density current *vs* ascorbic acid concentration

In case of the modified electrode the oxidation peak current attributed to the presence of AA in the electrolyte solution increased by comparison with that observed for the unmodified G electrode, which indicates that the perovskite material serves to improve the electrode's catalytic properties (data not shown). Thus, the presence of LaMnO<sub>3</sub> perovskite as a modifier facilitates the rate of the charge transfer. The increase of the intensity of the anodic current can be noticed as the concentration of AA becomes higher. These results constitute the premises for further investigations of the possibility to use this electrode as an ascorbic-acid sensor. Also, the capacitance of the perovskite-modified G electrode was obtained from the slope of the linear dependence of the capacitive current density *versus* the scan rate and was found to be  $3.96 \cdot 10^{-3}$  F cm<sup>-2</sup> (*versus*  $1.25 \cdot 10^{-3}$  F cm<sup>-2</sup> for the unmodified electrode).

## Conclusion

The LaMnO<sub>3</sub> perovskite material was deposited from suspension as a uniform film on the surface of graphite electrodes, which was confirmed by SEM imaging. The electrocatalytic behaviour of the modified electrodes in the presence of ascorbic acid indicates that LaMnO<sub>3</sub> is a promising material for the development of novel ascorbic acid sensors.

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