ELECTROCHEMICAL BEHAVIOUR OF LaMnO$_3$-MODIFIED GRAPHITE ELECTRODES

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Abstract

The electrochemical behaviour of LaMnO$_3$-modified graphite electrodes was studied using cyclic voltammetry. Potassium ferricyanide was employed as a probe to determine the electroactive surface area of LaMnO$_3$ modified electrodes and their diffusion coefficient. The electroactive surface area and the diffusion coefficient were calculated using the Randles-Sevcik equation.

Introduction

Perovskites are mixed-metal oxides of great interest for scientific researchers due to their optical, magnetic, catalytic, and electrical properties and not least because of their low price, high oxidation activity and thermal stability [1]. Perovskite ceramics are widely commercialized materials and have found numerous applications, including in automobile exhaust purification, fuel cells, solar cells and sensors [2,3,4,5].

In this paper the electrochemical behaviour of LaMnO$_3$-modified graphite electrodes is investigated as a preliminary stage in the identification of a suitable application.

Experimental

The electrochemical behaviour of the LaMnO$_3$ powder was investigated in a conventional three-electrode glass cell equipped with a Pt wire counter electrode, an Ag/AgCl (sat. KCl) reference electrode and a graphite (G) disk electrode (S = 0.28 cm^2) that served as substrate for a drop-casted thin layer of LaMnO$_3$. Prior to deposition the G electrode surface was polished and rinsed with double distilled water in an ultrasonic bath. The perovskite suspension was prepared by adding 10 mg LaMnO$_3$ powder in 500 μl DMF. After 30 min ultrasonication a volume of 15 μL suspension was carefully applied on the graphite electrode and allowed to air dry at room temperature. The modified G electrode was the working electrode and is denoted G_LMO.

Electrochemical experiments were carried out using the PGZ402 Voltalab potentiostat (Radiometer Analytical). Cyclic voltammograms were recorded on the unmodified G electrode as well as on the LaMnO$_3$-modified G electrode in 0.1 M KNO$_3$ electrolyte solution containing 4 mM potassium ferricyanide. The voltammograms obtained for the modified electrode were used to calculate its electroactive surface area and the diffusion coefficient (D), using the Randles-Sevcik equation [6,7]:

$$i_p = \left(2{,}69 \times 10^5\right) \times n^{3/2} \times A \times D^{1/2} \times C \times v^{1/2}$$

Where: i$_p$ = the peak current; n = the number of electrons involved in the redox process; A = the surface area of the working electrode; D = the diffusion coefficient of the electroactive species; C = the bulk concentration of the electroactive species and v = the scan rate.

All reagents were of analytical grade and were used as received without further purification. All potentials are referenced to the Ag/AgCl (sat. KCl) reference electrode.

Results and discussion

The voltammetry signals of $Fe(CN)_6^{3-/4-}$ at the modified graphite electrode were compared to the signals of the bare graphite electrode (Figure 1). The G_LMO response is the most intense and it can be associated with the large electroactive surface area (0.36 *vs.* 0.09 cm^2) calculated using the Randles–Sevcik equation. The perovskite deposition enhances the electron transfer rate due to the reation sites it provides.
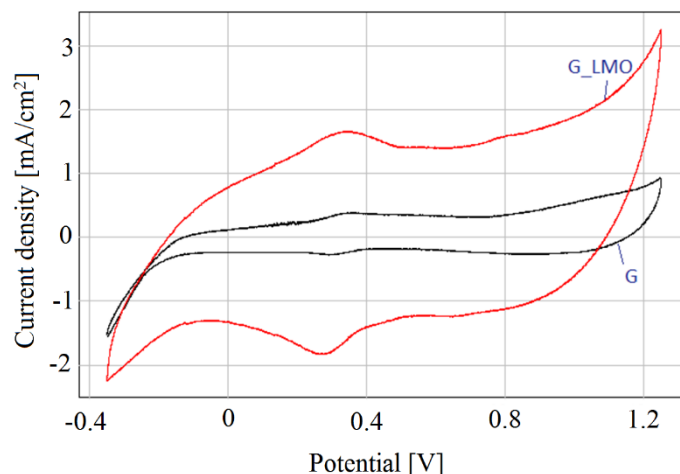

Figure 1. Cyclic voltammograms obtained in 1 M KNO_3 solution supporting electrolyte containing 4 mM $K_3Fe(CN)_6$, at 25 mVs^{-1}, for perovskite-modified graphite electrode (G_LMO) compared with the bare graphite electrode (G)

The diffusion coefficients for the two electrodes, in case of the ferrous/ferric redox couple at 298 K, were calculated based on the slope of the plot of the current density *vs.* the square root of the scan rate. Figure 2 shows the plot of the current density *vs.* the square root of scan rate obtained for the G_LMO electrode. The redox peak currents are proportional to the square root of the scan rate indicating a diffusion controlled electron-transfer process. The diffusion coefficients for the two electrodes were: $1.127 \cdot 10^{-5}$ cm^2s^{-1} for the G_LMO electrode and $8.342 \cdot 10^{-7}$ cm^2s^{-1} for the bare G electrode. These results show an increase in the apparent diffusivity of the ferricyanide ions in case of the G_LMO electrode by comparison with the bare G electrode.
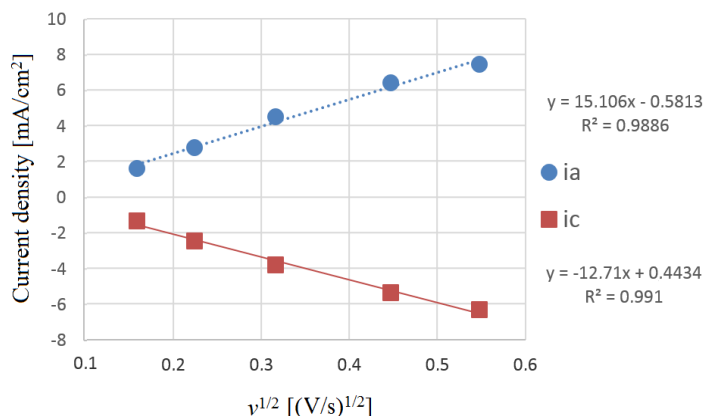

Figure 2. The plot of the current density *vs.* the square root of scan rate obtained for the G_LMO electrode. ia = anodic current density; ic = cathodic current density

Conclusion

$LaMnO_3$ was applied on the surface of a graphite electrode. The perovskite acted as an electrode modifier that enhanced the graphite electrode's electroactive surface area, which was calculated using the Randles–Sevcik equation. Furthermore, the perovskite material led to an increase in the apparent diffusivity of the ferricyanide ions.

Acknowledgements

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