

Interpretation of the Impedance of Ti/IrO₂ Electrodes using the Porous Two-phase Medium Model

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In general, IrO₂-based electrodes are prepared by thermal decomposition of an appropriate precursor solution onto a metallic titanium support, employing different methodologies. Independently of the method, the so-called “mud-cracked” coating is formed. These coatings exhibit a polycrystalline and rough surface, presenting microcracks and pores⁽¹⁾. From a technological point of view this morphologic configuration is desirable since it implies a high surface area, for example. However, from a fundamental point of view modelling the porous surface is an additional problem to be considered, which need a more detailed theoretical investigation and experimental support. In the study of DSAs as in other porous electrodes it is important to identify the main electroactive processes in different domains of applied voltage, and to assess the effects of the transport of electroactive species and of the catalytic surface reactivity. Electrochemical impedance is a powerful technique for obtaining such information, since the analysis of frequency resolved measurements enables one to separate the different electrochemical processes that compose the response.

This communication aims at present the analysis of the impedance of a porous Ti/IrO₂ electrode during double layer charging and under oxygen evolving reaction (OER) in acid medium. The impedance response was interpreted by a unique impedance relaxation function constructed with base on the porous model. Such impedance function account for the response in the double layer region as well as in the potential range where the OER takes place at the porous interface. The model used here is deduced elsewhere⁽²⁾ and the impedance equation obtained is mathematically analogous to the impedance of the transmission line pictured on the top of the Fig. 1.

The electrodes were prepared by the polymeric precursor method described elsewhere⁽³⁾. The impedance measurements was taken in the potential range of double layer charging ($0.15 \leq E \leq 1.15V_{(scc)}$) and the OER ($1.16 \leq E \leq 1.44V_{(scc)}$) in 1M HClO₄ solution.

Fig. 1 shows complex plane plots of the Ti/IrO₂ electrode in the region of the double layer charging and in the region of the OER. In the double layer charging process potential region (Fig. 1a) the spectrum shows the impedance response characteristic of the double layer charging of a porous electrochemical capacitor. In this complex plane one has two distinct regions of behaviour depending on the frequency. At high frequency region one has a line with slope close to 45°, termed Warburg-like impedance. On another hand, at low frequency wing one can see a line with inclination near than 90° that is a typical manifestation of a CPE. The high frequency part of the spectra remains practically unaffected by the potential. In the complex plane plots obtained in region of the OER the high frequency feature are observed while the arc in the low frequency wing is observed. At high potential for

the OER ($E = 1.40V$) one has a depressed arc as a consequence of the relation between the resistances (R_1 and R_3). In fact, all the spectra obtained were well fitted to the porous model proposed.

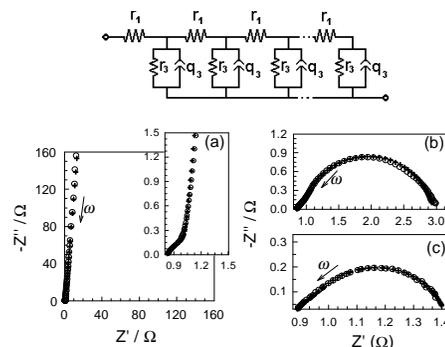


Fig. 1 – Complex plane plot representation of the impedance of the Ti/IrO₂ recorded at different potentials (a) 0.75; (b) 1.30 and (c) 1.40V. On the top: transmission line representing the impedance equation used in the fittings.

Fig. 2 shows the variation of the impedance parameters as a function of the applied potential. Analysing, these figures one can see that the capacitance of the electrode increases with increasing the applied potential displaying a plateau in the region of $0.60 \leq E \leq 1.10V$ where the charging are dominated by the presence of the solid state redox transition Ir(III)/Ir(IV)). The R_1 parameter (fig.2b) decreases to a stable value in the range of the double layer charging, That behaviour could be associated to the increase in the number of active sites in the coating surface or it could be associated to the resistance of protons transport along the pores wall.

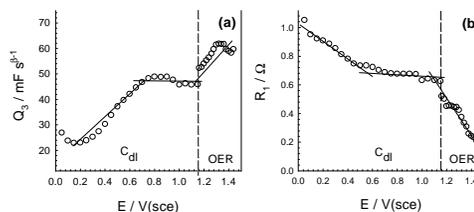


Fig. 2 – Impedance parameters of the Ti/IrO₂ as function of the applied potential. (a) capacitance (Q_3) and (b) distributed resistance (R_1).

In the region of OER ($E > 1.15V$) the R_1 parameter decreases as the potential increase while the capacitance increases up to a maximum value around of 60 mF at potential of 1.30V. The decrease in the capacitance for potentials higher than 1.30V could be related to the filling of the pores by the oxygen gas bubbles. On the other hand, the decrease of the R_1 parameter could be associated to the increase of the active sites in the coating.

The impedance of the Ti/IrO₂ was analysed with base on a model which contains physical information of the system (porosity) and the behaviour of impedance parameters with the applied potential were obtained.

References

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Acknowledgements: CNPq and FAPESP (97/07079-7).