PÔSTER - RESUMO - DISPOSITIVOS ELETRÔNICOS, ELETROQUÍMICOS, SUPERCAPACITORES E BATERIAS

DETECTION OF FARADAIC AND CAPACITIVE EVENTS DURING THE OXYGEN REDUCTION REACTION AT GLASSY CARBON ELECTRODES.

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The reduction of molecular oxygen dissolved in electrolytes is a common electrochemical process that often overlaps with other interfacial responses, making the interpretation of experimental data difficult. In general, its presence is avoided by using degassed electrolytes. However, the oxygen reduction reaction (ORR) is a fundamental step in fuel cells and has therefore been extensively studied in the field of electrocatalysis. In this context, the search for alternative catalytic pathways based on carbonaceous materials is particularly noteworthy. Voltammetric studies indicate that the ORR at solid carbon electrodes occurs in two steps, the first involving the adsorption of an intermediate species whose nature is still uncertain [1]. In this work, we investigate the impedimetric response of the ORR observed at glassy carbon (GC) electrodes when immersed in a non-degassed neutral electrolyte

containing 100 mM NaCl. For this purpose, we employ a differential analysis of the impedimetric response (GPE), which allows real-time detection of faradaic and capacitive processes as a function of the potential E, through the functions Alpha(E) and Cg(E), respectively [2,3]. Since this is an original methodology still under consolidation, we examine three factors that may influence the interpretation of the impedimetric response in three-electrode cells: the configuration of the field lines, the electrode size, and the quality of the GC. The results show that the Alpha(E) function exhibits two well-resolved minima separated by 0.25 V, indicating the occurrence of two faradaic events. This result is in strong contrast with the voltammetric curve, in which the two events appear in a convoluted and subtle manner. The well-resolved detection obtained by the GPE analysis is independent of the cell geometry or the provenance of the electrode. On the other hand, edge effects and non-homogeneous distributions of the field lines (simulated by COMSOL) affect the kinetics of the faradaic process. In the optimized geometric configuration, the faradaic events are detected only at frequencies lower than 40 Hz—evidencing their ionic origin—and are accompanied by an 11% increase in the double-layer capacitance, which confirms the occurrence of an adsorptive event. The quality of the interface, in terms of the distribution of relaxation times, is described by the maximum value exhibited by the Alpha(E) function and showed excellent correlation with the degree of homogeneity of the field lines of the investigated configurations. It was observed, however, that lower-quality GC electrodes exhibited a significant decrease in the Alpha function at frequencies below 500 Hz throughout the entire investigated potential range. The origin of this anomaly may be associated with the presence of impurities, since Raman spectra of the different electrodes did not indicate any structural differences among them [4].

Therefore, the GPE analysis of impedance spectra obtained in real time along a staircase potential scan provides a series of quantitative and unprecedented pieces of information about the electrochemical interface that help elucidate the mechanism underlying the ORR process.

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References:

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Palavras-chave: electrochemical impedance spectroscopy; generalized phase element; glassy carbon electrode; oxygen reduction.