Application of gas diffusion electrode made of polyaniline activated carbon for electrogeneration of hydrogen peroxide aiming the degradation of organic pollutants

ORAL/POSTER
Ph.D. Student: Y/N
Journal: NONE

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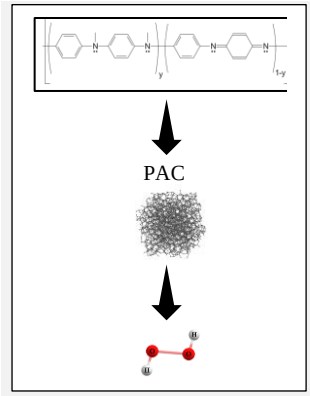

In this work, a novel activated carbon made of polyaniline (PAC) carbon was employed as the electroactive material for the fabrication of PAC gas diffusion electrode (GDE), applied for oxygen reduction reaction (ORR) aiming the the electrosynthesis of hydrogen peroxide (H_2O_2). The electrochemical study was carried out using a rotating ring-disk electrode (RRDE), applying different current densities. The results indicated that the material exhibits activity for ORR, particularly shifting the reaction to more positive potentials (-0.1 V). The optimal current density was 25 mA cm^{-2}, achieving a Faradaic efficiency of 8.1% and an energy consumption of 50 kWh kg^{-1}. This indicates that the PAC/GDE can effectively electro-generates H_2O_2, which can subsequently be applied for the degradation of organic compounds through advanced oxidative processes (POAs).

Introduction

Carbon-based materials have been extensively studied for the electrosynthesis hydrogen peroxide (H_2O_2), which is a versatily oxidant with several applications. Printex L6, Printex XE2B, and Vulcan stand out among the best carbons for this purpose. Activated carbons from new sources, especially those derived from polyaniline have been succesful applied in the field of supercapacitor, but they were not explored as active materials for GDE. Initially studied by Zornita *et al*. (2020), polyaniline-derived carbon (PAC) is of interest due to its amorphous structure, easy synthesis, low cost, and activation with KOH, which can result in higher efficiency in H_2O_2 generation. An alternative to explore the electrochemical properties of PAC is its the use in gas diffusion electrode (GDE), which allows for the triple interface (gas-solid-liquid). Since the main reactant (oxygen) is in gaseous form, the GDE is particularly suitable. Another advantage is that the GDE can be coupled with different electrochemical cells for the degradation of organic pollutants. One of the main processes used for electrochemical degradation is advanced oxidation processes (AOPs), which are based on the generation of hydroxyl radicals (•OH), with H_2O_2 being the primary precursor of the hydroxyl radical (Lima, et al., 2020; Zornitta, et al., 2020)

Material and Methods

The synthesis of the PAC material was described elsewhere (Zornitta et al., 2020[2]). To study the PAC material for H_2O_2 electrogeneration, a rotating ring-disk electrode (RRDE) was used, depositing a microfilm of the material with a loading of 25 μg cm^{-2}. The electrochemical behavior of the material was recorded using cyclic and linear voltammetry, as well as its performance in the oxygen reduction reaction (ORR) (electrochemical reaction for H_2O_2 generation). Subsequently, PAC was used to fabricate the GDE, where the material was homogeneously mixed with PTFE to ensure its mechanical stability. The GDE was prepared using a sample of 2.0 g (PAC / 20% PTFE), supported on carbon cloth. To study H_2O_2 electrogeneration, an electrochemical cell that allows gas entry at the cathode (GDE) was used, with a DSA® as the anode. Various current densities were applied in the system, and the Faradaic efficiency and energy consumption of each electrolysis were calculated to determine the optimal condition. The concentration of H_2O_2 was analyzed using ammonium molybdate[1], which reacts with H_2O_2 to form a yellow-colored complex. This complex was quantified using a Shimadzu UV-Vis 1800 spectrophotometer.

Results and Discussion

The electrochemical performance of PAC in the ORR is shown in Fig. 1(a), in which the lower part refers to the current detected at the disk where the microfilm of the material is deposited and where the ORR occurs, while the upper part records the current at the platinum ring, which corresponds to

the oxidation of H_2O_2.

The material exhibits activity for the ORR and the current detected at the ring indicates that H_2O_2 has been electrogenerated. The measured current and selectivity were lower than those observed for other carbons reported in the literature; however, the potential at which the ORR starts is shifted to more positive potentials (-0.1 V) compared to other materials (in general, around -0.4 V), indicating that PAC presents an energetic advantage in the generation of H_2O_2.

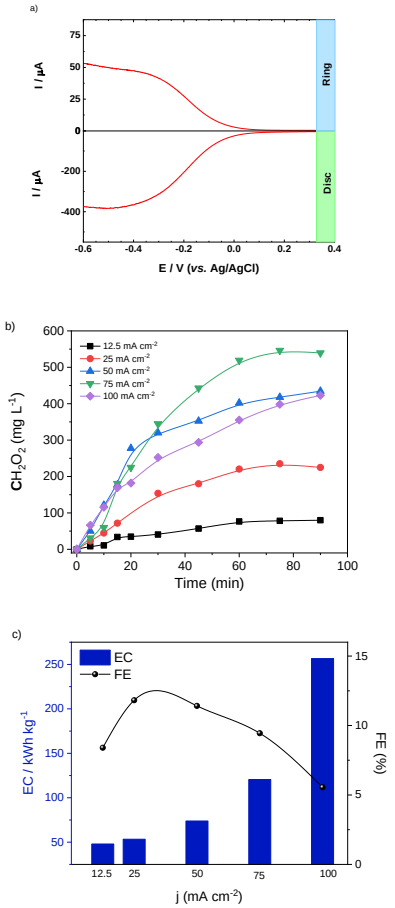

Figure 1. (a) Linear sweep voltammetry in O_2 for PAC using RRDE (b) Electro-generation of PAC GDE at different current densities for 90 minutes (c) Calculation of energy consumption and Faradaic efficiency for the applied current densities in H_2O_2 generation.

The performance of H_2O_2 electrogeneration by PAC-based GDE is presented in Fig. 1(b). At all current densities studied, the generation of H_2O_2 incresed up to 45 min and then remained constant. This behavior is attributed to the equilibrium between the H_2O_2 generation rate and the self-consumption rate of the excess H_2O_2. Increasing the applied current density to the GDE, the concentration of electrogenerated H_2O_2 also increase. However, at 100 mA cm^{-2}, the generation begins to decrease, indicating that the PAC/GDE demonstrates an optimal performance at lower current densities. The maximum H_2O_2 concentration was achieved at 75 mA cm^{-2}, reaching 540 mg L^{-1}. In order to determine the optimal current density for the PAC/GDE, it should be considered both energy consumption and Faradaic efficiency. As shown in Fig. 1(c), the specific energy consumption increases at higher current densities. Appling 12.5 and 25 mA cm^{-2} the specific energy consumption were quite similar (~ 50 kWh kg^{-1}). Faradaic efficiency followed the same trend observed in the electrochemical analysis of the oxygen reduction reaction (ORR). At lower current densities (correspondin to lower cell potentials), the PAC/GDE exhibits superior performance. For current densities of 12.5, 25, and 50 mA cm^{-2}, the Faradaic efficiencies were 8.4%, 8.1%, and 8.4%, respectively. Therefore, the electrode shows better activity at lower potentials by shifting the ORR.

Conclusions

The PAC material exhibits activity for the ORR and selectivity for H_2O_2, with its main contribution being the displacement of the reaction potential. The GDE fabricated with PAC is capable of electrogenerating H_2O_2 and, consistent with RRDE data, shows better performance at lower current densities due to lower cell potential values. The best current density was 25 mA cm^{-2}. Therefore, the PAC material is effective in the electrogeneration of H_2O_2, making it a promising candidate for future use in Advanced Oxidation Processes (AOPs).

Acknowledgments

FAPESP #2023/08720-4; 2022/12895-1; Federal University of São Carlos; University of São Paulo.

References

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