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Zeolitic imidazolate framework-Zn structure applied as catalyst of the Printex L6 carbon for H_2O_2 electrogeneration by using a Gas Diffusion Electrode

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In recent years, water treatment and purification focus on developing new, on-demand and decentralized technologies. In this sense, electrochemical flow reactors (EFR) using systems that contain gas diffusion electrode (GDE) for the electrogeneration of oxidants like hydrogen peroxide (H_2O_2) is promising. However, work that reports the investigation of novel electrode materials remains critical for improving efficiency and stability [1]. This study proposes the modification of carbon-based GDE with zeolitic imidazolate framework-Zn (ZIF-Zn) structure to optimize the oxygen reduction reaction (ORR) towards H_2O_2 production. We employed a previously established method for GDE synthesis to incorporate 0.5-2.0 wt% of a ZIF-Zn into a commercial carbon matrix Printex-L6 (CPL6). The modified GDE served as the cathode, while a commercial DSA®-Cl_2 electrode was used as anode in the EFR system studied elsewhere [2]. A semi-batch system with a 1L reservoir connected to the EFR was employed to evaluate the effects of varying pH (3 - 10) and cell potential (2.5 - 15.0 V) on H_2O_2 production performance. Additionally, reaction kinetics, current efficiency, and energy consumption were investigated. To understand the differences in surface properties between the unmodified and modified GDEs, electrochemical impedance spectroscopy (EIS) was performed. The investigation of ZIF-Zn content within the CPL6 revealed that 1.0 wt% of this catalyst offered the optimal modification for H_2O_2 production, compared to both higher (2.0 wt%) and lower (0.5 wt%) ZIF-Zn loadings. Among all test conditions, the ZIF-Zn/CPL6(1%) exhibited the

highest H_2O_2 concentration after 60 min. of electrolysis. At a cell potential of 10.0 V, the modified electrode achieved a superior current efficiency (23.9%) compared to the unmodified CPL6-GDE (12.3%). The current density experiments at 100 mA cm^{-2} revealed a plateau in H_2O_2 production for both electrodes (CPL6 and ZIF/CPL6(1%)) after 3 h. Prior to this plateau, a linear increase was observed, allowing for the definition of a kinetic system for H_2O_2 production. The apparent rate constant derived from the slopes of linear curves were 16.4 and 12.2 mg L^{-1} min^{-1} for ZIF-Zn/CPL6-GDE(1%) and CPL6-GDE, respectively. The modified GDE showed better performance at all tested pH values. Interestingly, the variation of H_2O_2 concentration by change the initial pH during electrolysis was minimal for both electrodes. The repeatability of the H_2O_2 production process by using ZIF-Zn/CPL6(1%)-GDE was confirmed by testing three electrodes prepared from the same batch, being an RSD of 13.6%. The EIS analysis, by Nyquist plots, indicated a porous material profile for both electrodes, as expected for GDEs. The Bode plot for the CPL6-GDE exhibited three distinct phase changes, which can be attributed to the ORR proceeding through multiple pathways. The first likely involves a two-electron transfer, generating H_2O_2, while the second can be the H_2O_2 reduction into H_2O. The third phases might correspond H_2O reduction, since this phase occurs at the same frequency for both electrodes. This multi-step process could explain the lower efficiency observed for the CPL6-GDE compared to the ZIF-Zn/CPL6(1%). In conclusion, this study demonstrates the successful application of ZIF-Zn for modifying commercially available CPL6 matrices to enhance the efficiency of GDE to H_2O_2 production via ORR. This represents a novel approach in GDE modification for this specific application, as evidenced by the lack of prior other studies. The findings contribute significantly to our understanding of how material modifications can influence for the H_2O_2 electrogeneration using GDE. This knowledge provides a valuable foundation for future research efforts aimed at optimizing electrocatalysts for improved performance and efficiency.

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