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Carbon-based gas diffusion electrodes for two electron oxygen reduction: mechanistic study and performance in organic and water-alcohol media in flow cells

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Hydrogen peroxide (H_2O_2) is an important chemical with growing demand, traditionally produced through the energy-intensive anthraquinone process. In contrast, electrochemical synthesis via the two-electron oxygen reduction reaction ($2e^-$-ORR) offers a sustainable alternative, operating under mild conditions and powered by renewable electricity [1]. Carbon-based materials, particularly Printex® L6 carbon (PL6C), are highly selective for $2e^-$-ORR due to their large surface area and oxygenated functional groups with recent studies demonstrating its efficiency for H_2O_2 electrosynthesis in both acidic and alkaline media [2]. While significant research has explored H_2O_2 electrogeneration in aqueous media, the feasibility in methanol and water-alcohol mixtures remains underexplored. The electrosynthesis of H_2O_2 in methanol could offer advantages for processes that already use methanol. In this frame, this study demonstrates the H_2O_2 electrogeneration in organic media and water-methanol mixtures (30% methanol and 50% methanol) using a 3D-printed flow cell equipped with a PL6C-GDE. Electrochemical characterization using the rotating disk electrode technique and electron paramagnetic resonance (EPR) spectroscopy with spin trapping were used to investigate reaction mechanisms. As result, linear sweep voltammetry recorded in methanol showed a significant increase in cathodic current compared to water and methanol-water mixtures, suggesting its participation in the ORR process. Interesting, the LSV curves for water-methanol were similar to water, suggesting that presence of 30 and 50% of methanol does not significantly alter the electrochemical behavior. H_2O_2 electrosynthesis was tested in two cell configurations - divided and undivided - using the GDE as cathode and a Ti/RuO_2-TiO_2 dimensionally stable anode. In the divided system, higher Faradaic efficiency (FE) was observed in aqueous solution, while methanol and its mixtures resulted in lower FE yields. Although the kinetics for H_2O_2 production were similar in both water and methanol, energy consumption was higher for methanol. In the undivided reactor, however, the production of H_2O_2 in methanol increased, with FE approaching that of the aqueous solution. This can be due to lower overpotentials in the undivided system, resulting from the reduced distance between electrodes, as well as the suppression hydrogen evolution and anodic scavenger effects, which are typically observed in water. Moreover, in the divided system, FE for aqueous solution was lower compared to undivided one, as expected, since H_2O_2 consumption in anodic reactions is avoided in the divided reactor. Finally, EPR analysis helped to elucidate the mechanisms involved, identifying the formation of different radical species in water and methanol media, which directly influence the reactions for the hydrogen peroxide formation. These findings highlight the potential for *in situ* H_2O_2 production in organic and mixed solvent systems.

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