Generation of persulfate applying a novel electrochemical flow reactor with a NETmix static mixer

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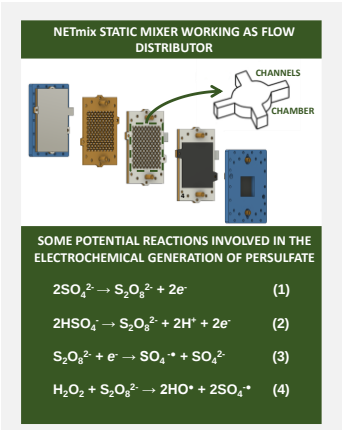

This work focused on the application of an innovative electrochemical flow reactor for the generation of persulfate ($S_2O_8^{2-}$) from sulfuric acid (H_2SO_4) oxidation. The new reactor integrates a newly developed static mixer named NETmix, which stands out for its ability to enhance mass transport properties. A boron-doped diamond (BDD) anode was applied. Two reactor configurations were tested: single and double-compartment. Moreover, the generation of $S_2O_8^{2-}$ was compared to that achieved in some electrochemical reactors reported in the literature. The new reactor demonstrated the ability to enhance the $S_2O_8^{2-}$ generation, particularly for the double-compartment configuration, minimizing the cathodic decomposition of $S_2O_8^{2-}$. Moreover, it showed superior performance compared to other reactors documented in the literature. After 120 min of reaction at a current density of 100 mA·cm^{-2}, the $S_2O_8^{2-}$ production was 126 mM, and the current efficiency was 67%.

Introduction

Over the past few decades, electrochemical research has placed great emphasis on electrode materials and catalytic properties. More recently, a rising interest in the design and construction of novel electrochemical flow reactors appeared due to the increasing demand for more efficient and industrially adapted processes. Electrochemical flow reactors can be employed to carry out a multitude of processes, including the generation of strong oxidants (H_2O_2, $S_2O_8^{2-}$), chemicals, and fuels, as also for environmental remediation purposes.

The electrochemical generation of $S_2O_8^{2-}$ occurs through the oxidation of sulfate species, such as sulfate ion (SO_4^{2-}) and hydrogen sulfate (HSO_4^-), at the anode surface (Equations 1 and 2 of Graphical Abstract), simultaneously with several side reactions. In this regard, the generated $S_2O_8^{2-}$ may decompose at the cathode surface (Equation 3) or interact with generated scavenger species, such as hydrogen peroxide (H_2O_2) (Equation 4). This decreases the production of $S_2O_8^{2-}$ and the current efficiency (CE) of the process [2].

The design of the electrochemical flow reactor can help to improve the mass transport of species to and from the electrodes, ultimately enhancing the process's productivity. Furthermore, the configuration of the electrochemical flow reactor can comprise the use of an ionic exchange membrane (IEM) to separate the electrode compartments, hence preventing the generated $S_2O_8^{2-}$ from reaching the cathode and undergoing undesired reactions.

In this study, a cutting-edge electrochemical flow reactor with a NETmix static mixer working as a flow distributor was developed and applied to the generation of $S_2O_8^{2-}$ from sulfuric acid (H_2SO_4) using a boron-doped diamond (BDD) anode. The NETmix consists of a 2D network structure that combines cylindrical chambers interconnected by prismatic channels (see Graphical Abstract). This novel static mixer provides outstanding mass transport rates [3]. The electrochemical generation of $S_2O_8^{2-}$ was carried out using single or double-compartment reactor configurations. Furthermore, the $S_2O_8^{2-}$ generation in the new reactor was compared to that in other reactors reported in the literature.

Material and Methods

Besides the BDD anode, the electrochemical reactor was equipped with a stainless steel (SS) cathode and, in trials regarding the double-compartment configuration, a Nafion 117 proton exchange membrane (PEM). 1 M H_2SO_4 was used as substrate and supporting electrolyte. Trials were carried out in semi-batch mode. A flow rate (Q) of 40 L h^{-1} was applied (in each compartment for the double-compartment configuration), and the temperature (T) was kept at 20±2°C. A current density (j) of 100 mA cm^{-2} was provided. The concentration of $S_2O_8^{2-}$ was measured using the iodometric titration method, as reported in Castro et al. [4].

Results and Discussion

Figure 1 shows the effect of the electrochemical reactor configuration (single or double-compartment)

in terms of generated $S_2O_8^{2-}$ (Figure 1a) and CE (Figure 1b). At 360 min of reaction, the reactor with the double-compartment yielded a maximum of 348 mM of $S_2O_8^{2-}$. This value was 3.5 times superior compared to that obtained for the single-compartment configuration. Furthermore, the CE increased by 43% (from 18% to 61%) when the electrode compartments were separated. These results indicate that the decomposition of the $S_2O_8^{2-}$ occured at the cathode compartment in the single-compartment configuration.

Table 1 displays the performance of the new electrochemical flow reactor as regards $S_2O_8^{2-}$ generation compared to that of some electrochemical flow reactors reported in the literature. Castro et al. [4] achieved a higher $S_2O_8^{2-}$ generation but using a *j* 3 times higher. The $S_2O_8^{2-}$ generation was lower in Silva et al. [5]. The better performance of the novel reactor can be mainly attributed to its mass transfer properties as a result of the use of a NETmix static mixer as a flow distributor. The NETmix promotes convective mixing and the development of a laminar chaotic flow regime.

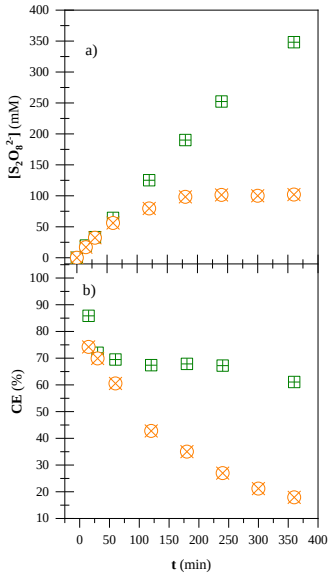

Figure 1. Effect of reactor configuration - single-compartment (⊗) *versus* double-compartment (⊞) - on the (a) generation of $S_2O_8^{2-}$ and (b) current efficiency (CE).

Table 1. Electrochemical generation of $S_2O_8^{2-}$ in various electrochemical flow reactors.

Anode	Membrane	$[SO_4^{2-}]$ (M)	*j* (mA cm^{-2})	$[S_2O_8^{2-}]$ (mM) (120 min)	CE (%)	Reference
BDD	-	1.0	100	80	43	This work
BDD	Nafion 117	1.0	100	126	68	This work
BDD	Nafion 117	1.0	300	161	57	[4]
BDD	-	0.5	60	2.1	20	[5]

Conclusions

The cutting-edge electrochemical flow reactor with a NETmix static mixer proved to promote the $S_2O_8^{2-}$ generation, especially using the double-compartment configuration, for which the cathodic decomposition of $S_2O_8^{2-}$ was minimized. The $S_2O_8^{2-}$ production was 126 mM and the CE was 67% after 120 min of reaction at 100 mA·cm^{-2} using the double-compartment configuration. The new reactor outperformed other reactors reported in the literature.

Acknowledgments

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References

[1] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, *Applied Catalysis B,* 202 (2017) 217.
[2] S.Q. Yang, Y.H. Cui, Y.Y. Liu, Z.Q. Liu, X.Y. Li, *Separation and Purification Technologies*, 207 (2018) 461.
[3] D.F.S Morais, J.C.B. Lopes, M.M. Dias, V.J.P Vilar, F.C. Moreira, *Chemical Engineering Journal*, 481 (2024) 148244.
[4] M.P. Castro, M.A. Montiel, I.F. Mena, J. Gäbler, H. King, C. Sáez, M.A. Rodrigo, *Separation and Purification Technology*, 320 (2023) 124118.
[5] K.N.O Silva, K.C.F Araújo, D.R. da Silva, C.A. Martínez-Huitle, E.V. dos Santos, *Journal of Electroanalytical Chemistry*, 895 (2021) 115498.